

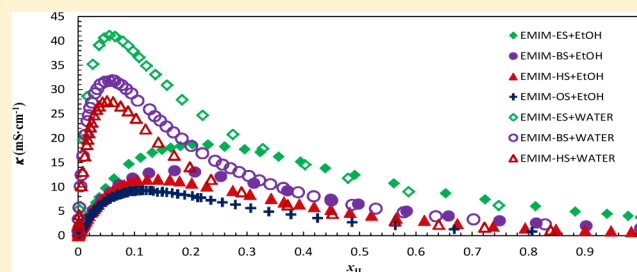
Electrical Conductivity of Seven Binary Systems Containing 1-Ethyl-3-methyl Imidazolium Alkyl Sulfate Ionic Liquids with Water or Ethanol at Four Temperatures

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ABSTRACT: We present experimental measurements of specific electrical (or ionic) conductivity of seven binary systems of 1-ethyl-3-methyl imidazolium alkyl sulfate (EMIM- C_n S) with water or ethanol. Electrical conductivity was measured at 298.15 K in all ranges of concentrations and selected mixtures also at 288.15, 308.15, and 318.15 K. The alkyl chains of the anions used are ethyl (EMIM-ES), butyl (EMIM-BS), hexyl (EMIM-HS), and, only for mixtures with ethanol, octyl (EMIM-OS). Let us note that the four ionic liquids (ILs) measured are miscible in water and ethanol at those temperatures and atmospheric pressure in all ranges of concentration, but EMIM-OS jellifies for a given range of concentration with water. We compare the measured data in terms of the alkyl chain length and solvent nature. Data are compared with previously scarce results for these same systems and also for other aqueous and ethanol mixtures with ILs. In addition, we verify that our data fit the universal theoretical expression with no fitting parameters given by the pseudolattice-based Bahe–Varela model, except for IL concentrated mixtures. To fit well all ranges of concentrations, we add to the original equation two phenomenological terms with one fitting parameter each. Finally, we calculate the molar conductivity and fit it successfully with an expression derived from Onsager theory.



INTRODUCTION

Ionic liquids (ILs) are salts with melting temperatures below 100 °C (and usually below room temperature); in fact, they are also known as room temperature ionic liquids (RTILs). One or both ions are large, and usually the cation is organic, has a low degree of symmetry, and presents an alkyl chain with a variable (but majority of times even) number of carbon atoms. For this reason, electrostatic anion–cation interactions are weak enough, and hence they are in a liquid state at room temperature. The length of the alkyl chain of the cation (or of the anion such as in the IL family studied in this paper) cannot be too large because the van der Waals forces would increase the melting temperature above 100 °C. So there is an optimal length of that alkyl tail (about 5 carbon atoms) to obtain the minimum melting point in a given family of ILs. The first IL was discovered in 1914 by Paul Walden (the ethylammonium nitrate), but the systematic study of their properties began in the present century with the discovery of the imidazolium- and pyridinium-based ILs.¹ The interest of the scientific community comes from the peculiar properties all ILs present, such as: good selective solvents for organic and inorganic compounds, lack of vapor pressure, high electrical conductivity, broad electrochemical window, and high thermal and electrochemical stability. Different combinations of the multiple anions and cations lead to billions of possible ILs with very different physicochemical properties. So we can design a given IL with the

appropriate set of properties according to our purposes. All these characteristics make ionic liquids promising compounds to develop Green Chemistry projects. Thus, from the beginning, ILs have been proposed to be used in batteries, organic synthesis, extractions, alloy electro-deposition, lubricants, as well as “green solvent” replacements for volatile organic compounds (VOCs).²

Among the numerous proposed industrial applications of ionic liquids, their use to improve electrochemical processes is one of the most interesting.³ To do that, it is absolutely necessary to know the electrical conductivity of the different ILs, both pure and mixed with different solvents, including ethanol or water. This is especially important because the solvent addition dramatically diminishes IL viscosity,⁴ and hence it increases greatly their electrical conductivity.⁵ Due to the lack of predicting models, the only way to know the physical properties of the IL mixtures is experimentally, but before 2004 these data were very scarce.⁶ Since then, many papers have been published with experimental measurements on mixtures of ionic liquids with different kinds of solvents such as water, ethanol, aromatic compounds, or other ionic liquids, and the number of published papers is continuously growing;⁷

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however, systematic experimental investigation in many more IL families and solvents is needed. Respecting the electrical conductivity of binary systems formed by any IL with water or ethanol, we have found only eight papers reporting experimental measurements,^{8–15} which are clearly very few taking into account the huge number of ILs available.

In this article, we present experimental measurements of specific electrical (or ionic) conductivity on seven binary mixtures of 1-ethyl-3-methyl imidazolium alkyl sulfate (EMIM- C_n S) with water or ethanol. The alkyl chains of the sulfate anion studied are ethyl (EMIM-ES), butyl (EMIM-BS), hexyl (EMIM-HS), and octyl (EMIM-OS); all of them are miscible with water and ethanol at all ranges of concentrations at room temperature. These compounds are commercially known as ECOENG 21n, n being the number of carbon atoms in the alkyl chain. Electrical conductivity was measured for all concentrations at 298.15 K, while ten selected mixtures were also measured at 288.15, 308.15, and 318.15 K. Let us note that in a given composition range (for IL molar fraction between 0.14 and 0.28) the aqueous mixtures of EMIM-OS jellyfy, as we published recently.¹⁶ Finally, it is important to note that this family of ILs is one of the most promising for a number of electrochemical applications because, among other causes, it is totally halogen free,¹⁷ and also members of this family have been proposed for deterpenation of oils^{18,19} or as a reaction matrix for the synthesis of coumarins.²⁰ In spite of their promising applied uses, not many papers have been devoted to the experimental study of alkyl sulfate based ILs. Thus, for pure compounds, density data have been published in some papers for different EMIM- C_n S^{21–24} and also in function of pressure.²⁵ Also the surface tensions of some members of the alkyl sulfate IL family have been studied with some extension.^{16,24,26–28} Other physical magnitudes have received lower attention in the literature, thus we have found only three papers devoted to viscosity measurements, two of them at ambient pressure^{23,24} and another one reporting its effect on viscosity.²⁹ Finally, we found just one published paper giving refractive index data.²²

This paper complements two recently published ones by us, where we presented surface tension¹⁶ and density²¹ for the same systems presented here at 298.15 K. The goals of this work are to study the effects of the alkyl chain length of the sulfate anion in the electrical conductivity and also the influence of the solvent.

EXPERIMENTAL SECTION

Electrical conductivity was measured using a Crison GLP+ conductivimeter, which has a resolution about 1% of the measured value with the appropriate measurement cell. It uses a constant 500 Hz ac current in all measurement ranges. The samples were thermostatted in an external bath with an accuracy of 0.1 K. Details of the electrical conductivity apparatus and measurement procedure were given before.³⁰ The EMIM-ES was purchased from IoLiTec and the three others from Merck. Their purities are given in Table 1, and the ILs were used as received without any further purification. The water content of the four ILs is lower than 1000 ppm, as certified by the dealer and measured by us using a Karl Fisher 701 KF Titrino coulometer, while the halogen impurities are lower than 100 ppm for EMIM-ES and “not detected” for the other three ILs used. The exact value of original water content for each pure IL is included in Table 1. Due to the hygroscopic character of these ILs, the original bottles were open and mixed with water (or ethanol) into a dry chamber, with relative humidity grade lower

Table 1. Purity, Molar Mass (M), Water Weight Fraction Measured with a Karl Fisher Titrator (w), Density (ρ) from Ref 21, and Electrical Conductivity (κ) of the Chemicals Used at 298.15 K^a

	purity	$M/\text{g}\cdot\text{mol}^{-1}$	$10^6 w$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\kappa/\text{S}\cdot\text{m}^{-1}$
EMIM-ES	99%	236.159	200	1238.30	0.380
EMIM-BS	98%	264.35	1200	1175.65	0.1498
EMIM-HS	98%	292.40	600	1129.60	0.0789
EMIM-OS	98%	320.46	<1000	1093.75	0.0428
water	Milli-Q	18.02	-	997.00	0.00264
ethanol	99.5%	46.07	2000	785.85	0.00003

^aExperimental uncertainties are $\pm 0.05 \text{ kg}\cdot\text{m}^{-3}$ for ρ and $\pm 1\% \text{ S}\cdot\text{m}^{-1}$ for κ .

than 15%. This humidity grade, and the speed of the mixing process, ensures that our original ILs were not contaminated with moisture. Take into account that these ILs are among the most hygroscopic ones, as some of us measured quantitatively.³¹ The mixtures were bottled and sealed before taking them out of the dry chamber. The water used for the mixtures was Milli-Q grade, while the ethanol is from Panreac. Besides purity and water content of the six pure compounds used, in Table 1 we show their molecular mass, M , density, ρ (published in ref 21), and specific electrical conductivity, κ . We have not found previously published κ data for the pure ILs used³² except for the EMIM-ES^{5,11,15,33} observing a reasonable grade of agreement between both sets of data, taking into account the high hygroscopic character of EMIM-ES.³¹ We found data for some other ethyl sulfate ILs but with different organic cations; thus EMIM-ES has a κ value very similar to 1-ethyl-1-methylpyrrolidinium-ES but much higher than both 1-ethyl-1-methylpiperidinium-ES and 4-ethyl-4-methylmorpholin-4-ium-ES.¹⁷ With respect to data about mixtures of any alkyl sulfate IL with any solvent, we have found only two papers in the literature, one presenting data for aqueous mixtures of alkyl sulfate ILs different from those presented here and in the diluted range ($c < 0.1 \text{ mol}\cdot\text{kg}^{-1}$)²⁸ and another one presenting molar conductivities for EMIM-ES with water, acetonitrile, and dichloromethane but only for very diluted mixtures (with $c < 0.005 \text{ mol}\cdot\text{L}^{-1}$).³⁴ Comparison among data presented in this last paper and ours is not possible because we have not measured so diluted mixtures, our data being for $c > 0.09 \text{ mol}\cdot\text{L}^{-1}$.

RESULTS AND DISCUSSION

In Table 2 we show the electrical conductivity data, κ , at 298.15 K for the three EMIM- C_n S ILs in aqueous mixtures at all concentrations measured (expressed this last as molar fraction, x_{IL} , and molarity, c), while Table 3 include the measured data for all mixtures with ethanol. Figure 1 shows κ for mixtures with (a) water, (b) ethanol, and (c) both solvents with $x_{\text{IL}} > 0.3$. As observed in this last figure, for low solvent concentration, data measured present similar values for water as for ethanol. However, above $x_{\text{IL}} \approx 0.3$ the κ value of the aqueous solutions increases much faster for decreasing IL content than the corresponding ones with ethanol. All systems present a maximum of conductivity at a given concentration, but the composition and absolute value are different for both solvents. Thus, for the aqueous mixtures the molar fraction where the maximum in κ appears is the same for the four IL systems ($x_{\text{IL}} = 0.06$, which represents about 50% of mass in water). In contrast, for the ethanol systems the IL concentration where

Table 2. Electrical Conductivity for the Aqueous Mixtures of the EMIM- C_n S Ionic Liquids Studied with $n = 2$ (Ethyl), $n = 4$ (Butyl), and $n = 6$ (Hexyl) at 298.15 K

x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$
EMIM-ES + water						EMIM-BS + water					
1.0000	5.241	3.80	0.0976	2.810	37.9	0.2705	3.674	13.82	0.0186	0.848	24.7
0.7471	5.084	6.21	0.0887	2.670	39.0	0.2563	3.625	14.58	0.0166	0.771	23.5
0.5867	4.926	9.05	0.0792	2.505	39.9	0.2431	3.577	15.37	0.0127	0.614	20.7
0.4794	4.770	11.81	0.0653	2.233	40.9	0.2208	3.484	16.88	0.0086	0.433	16.31
0.4026	4.616	14.59	0.0554	2.009	41.1	0.2009	3.390	18.41	0.0057	0.298	12.43
0.3278	4.412	17.88	0.0462	1.777	40.6	0.1839	3.298	19.91	0.0043	0.225	10.12
0.2745	4.217	20.8	0.0370	1.514	39.1	0.1692	3.208	21.2	0.0021	0.112	5.76
0.2210	3.955	24.7	0.0258	1.147	35.2	0.1566	3.122	22.4	0.0011	0.060	3.35
0.1844	3.719	27.9	0.0164	0.782	28.6	0.1455	3.040	23.6	0.0003	0.016	0.994
0.1574	3.501	30.9	0.0088	0.450	19.78						
0.1371	3.304	33.1	0.0016	0.089	5.40						
0.1210	3.124	34.9	0.0000	0.000	0.0264						
0.1081	2.959	36.6									
EMIM-BS + water						EMIM-HS + water					
1.0000	4.447	1.496	0.1359	2.962	24.5	1.0000	3.864	0.789	0.0510	1.684	27.7
0.8295	4.378	2.31	0.1271	2.883	25.9	0.8393	3.813	1.200	0.0431	1.516	27.4
0.7023	4.306	3.33	0.1057	2.664	27.7	0.7218	3.764	1.746	0.0371	1.375	26.6
0.6353	4.259	3.99	0.0946	2.533	29.2	0.6403	3.720	2.29	0.0325	1.256	25.9
0.5782	4.210	4.79	0.0853	2.405	30.1	0.5626	3.667	3.03	0.0282	1.134	24.8
0.5288	4.160	5.54	0.0773	2.284	30.9	0.4513	3.566	4.57	0.0244	1.017	23.3
0.4868	4.111	6.32	0.0706	2.171	31.3	0.3718	3.462	6.31	0.0214	0.919	22.3
0.4498	4.061	7.22	0.0646	2.064	31.8	0.2902	3.308	9.01	0.0190	0.838	21.1
0.4185	4.013	8.07	0.0551	1.875	31.7	0.2360	3.159	11.53	0.0168	0.759	19.83
0.3907	3.965	8.88	0.0478	1.713	31.6	0.1981	3.019	14.13	0.0150	0.692	18.72
0.3645	3.915	9.78	0.0399	1.515	31.1	0.1701	2.888	16.51	0.0115	0.551	16.36
0.3415	3.866	10.57	0.0339	1.352	30.1	0.1422	2.724	19.17	0.0078	0.390	13.19
0.3217	3.819	11.34	0.0295	1.218	29.2	0.1194	2.556	21.9	0.0052	0.269	10.22
0.3031	3.771	12.24	0.0243	1.052	27.3	0.1026	2.405	24.1	0.0017	0.090	4.28
0.2860	3.722	13.04	0.0211	0.941	26.2	0.0881	2.250	25.6	0.0010	0.053	2.71
						0.0753	2.086	26.6	0.0007	0.037	1.983
						0.0620	1.883	27.5	0.0003	0.015	0.877

the κ maximum appears decreases with the alkyl chain increase, thus it appears at $x_{\text{IL}} = 0.22$ for ethyl ($\approx 40\%$ of mass in ethanol), at $x_{\text{IL}} = 0.17$ for butyl, at $x_{\text{IL}} = 0.14$ for hexyl, and at $x_{\text{IL}} = 0.13$ for octyl ($\approx 55\%$ of mass in ethanol). We can also observe that in aqueous systems the electrical conductivity value of the pure EMIM-ES increases more than 10 times, about 20 times for EMIM-BS, and more than 30 times for systems with EMIM-HS. In contrast, for ethanol mixtures the pure EMIM-ES value increases only 5 times, EMIM-BS nearly 9 times, EMIM-HS about 15 times, and EMIM-OS about 20 times. The peak of κ at a given concentration had already been observed before for other IL binary mixtures,^{5,10–14} including the family of $C_n\text{MIM-BF}_4$ with water¹² and with ethanol.¹³ For these last systems, the peak is also much higher for aqueous mixtures than for the corresponding ones with ethanol, even with a major difference between both maximum values. Thus, κ maximum value increases about 15 times for BMIM- BF_4 + water and only 5 times for the same IL with ethanol. In general, for aqueous systems maximum κ value is nearly double for $C_n\text{MIM-BF}_4$ than for EMIM- $C_n\text{S}$ (for the same n value), while they are similar for ethanol mixtures. Finally, it is interesting to note that for the $C_n\text{MIM-BF}_4$ systems the ionic liquid molar fraction where the maximum in κ appears decreases as the alkyl chain length increases for both solvents.

The differences observed in the electrical conductivity curves depending on the solvent used for both systems can

be explained based on the well-known different microscopic structures of IL mixtures with water and with ethanol. As proved by molecular dynamics (MD) simulations, water molecules are largely clusterized in bulk IL–water mixtures^{35,36} at high IL concentration, offering the ions a favorable environment for hopping processes and for fast diffusion processes in large water regions at intermediate concentrations. In fact, as proved in MD simulations,³⁶ the mixture is essentially formed by isolated water molecules or those belonging to small clusters formed by no more than four or five molecules; however, water aggregates with larger sizes appear soon, and over a water molecule concentration of 85% a complete water network is formed, with most water molecules belonging to a cluster whose size is very close to the total number of water molecules in the mixture and only a few isolated or forming small independent water clusters. Contrarily, ethanol molecules are currently known to be mostly dispersed in small clusters in alcohol–IL mixtures, those clusters of 2 molecules (dimers) being dominant.^{35–38} MD simulations also show that, although at intermediate alcohol concentrations small clusters appear, an alcohol network is never formed,³⁶ and therefore ethanol mixtures of ILs do not offer such a favorable environment for charge transport as that in aqueous IL mixtures. Therefore, given that a water network is readily formed in these last mixtures, the concentration at which the conductivity maximum is reached is expected to be essentially independent of water concentration and only slightly dependent on the nature of the

Table 3. Electrical Conductivity for the Binary Mixtures with Ethanol of EMIM- C_n S with $n = 2$ (Ethyl), $n = 4$ (Butyl), $n = 6$ (Hexyl) and $n = 8$ (Octyl) at 298.15 K

x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$
EMIM-ES + ethanol						EMIM-HS + ethanol					
1.0000	5.241	3.81	0.1640	2.060	18.07	0.5650	3.299	3.60	0.0238	0.377	4.85
0.9769	5.205	4.05	0.1489	1.918	17.59	0.5211	3.208	4.20	0.0195	0.312	4.12
0.9394	5.144	4.50	0.1315	1.744	17.03	0.4827	3.119	4.79	0.0164	0.265	3.60
0.8829	5.043	4.95	0.1111	1.527	16.00	0.4489	3.033	5.38	0.0140	0.229	3.21
0.8123	4.904	6.04	0.0899	1.285	14.68	0.4190	2.951	5.92	0.0123	0.201	2.88
0.7229	4.704	7.44	0.0635	0.954	11.76	0.3928	2.872	6.45	0.0107	0.177	2.57
0.6529	4.523	8.72	0.0486	0.751	9.75	0.3655	2.784	6.91	0.0096	0.158	2.35
0.5607	4.245	10.73	0.0374	0.590	7.91	0.3427	2.705	7.60	0.0085	0.141	2.16
0.4912	3.997	12.49	0.0314	0.502	6.79	0.3052	2.561	8.46	0.0075	0.124	1.918
0.4388	3.784	13.83	0.0248	0.402	5.63	0.2746	2.430	9.25	0.0066	0.110	1.738
0.3948	3.584	15.19	0.0187	0.307	4.45	0.2285	2.203	10.16	0.0058	0.097	1.540
0.3561	3.391	16.21	0.0149	0.247	3.71	0.2018	2.052	10.79	0.0045	0.076	1.270
0.3234	3.212	17.13	0.0093	0.155	2.46	0.1803	1.917	11.20	0.0036	0.060	1.063
0.2958	3.049	17.72	0.0071	0.120	2.02	0.1627	1.797	11.46	0.0029	0.049	0.904
0.2604	2.820	18.28	0.0044	0.074	1.369	0.1418	1.641	11.56	0.0021	0.036	0.714
0.2307	2.610	18.70	0.0013	0.021	0.530	0.1222	1.481	11.53	0.0017	0.029	0.595
0.2030	2.395	18.70	0.0000	0.000	0.0003	0.1061	1.337	11.28	0.0014	0.024	0.516
0.1817	2.217	18.39				0.0974	1.255	11.01	0.0011	0.019	0.440
EMIM-BS + ethanol						0.0899	1.180	10.74	0.0008	0.014	0.344
1.0000	4.447	1.501	0.2537	2.533	12.12	0.0819	1.098	10.40	0.0006	0.011	0.268
0.9027	4.329	1.99	0.2074	2.243	13.04	0.0752	1.026	10.03	0.0004	0.006	0.171
0.8141	4.202	2.57	0.1712	1.981	13.33	0.0693	0.961	9.71	0.0002	0.004	0.115
EMIM-OS + ethanol						1.0000	3.414	0.428	0.1022	1.242	9.26
0.7486	4.096	3.02	0.1258	1.593	12.83	0.8062	3.259	0.840	0.0920	1.150	9.24
0.6581	3.926	4.01	0.0968	1.305	11.79	0.6680	3.110	1.336	0.0821	1.057	8.91
0.5835	3.761	5.01	0.0565	0.835	8.82	0.5637	2.959	2.07	0.0697	0.931	8.49
0.4978	3.534	6.47	0.0425	0.649	7.43	0.4865	2.821	2.79	0.0605	0.832	8.03
0.4489	3.382	7.45	0.0270	0.429	5.14	0.4254	2.692	3.59	0.0533	0.750	7.72
0.3720	3.102	9.20	0.0723	1.030	10.46	0.3780	2.574	4.34	0.0455	0.657	6.96
0.3123	2.840	10.73	0.0135	0.223	2.87	0.3387	2.463	4.94	0.0353	0.528	6.05
x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	x_1	$c/\text{mol}\cdot\text{L}^{-1}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	0.3064	2.359	5.67	0.0287	0.439	5.27
EMIM-HS + ethanol						0.2795	2.263	6.38	0.0208	0.327	4.22
1.0000	3.863	0.798	0.0608	0.863	9.09	0.2561	2.170	6.84	0.0138	0.223	3.13
0.9826	3.849	0.833	0.0540	0.781	8.49	0.2356	2.082	7.28	0.0117	0.191	2.80
0.9467	3.819	0.958	0.0485	0.712	7.99	0.2181	1.999	7.81	0.0078	0.129	1.576
0.9006	3.774	1.099	0.0439	0.654	7.47	0.2124	1.971	7.80	0.0049	0.082	1.130
0.8488	3.718	1.293	0.0401	0.603	7.04	0.1763	1.775	8.56	0.0035	0.060	0.894
0.7941	3.653	1.549	0.0357	0.544	6.40	0.1501	1.608	9.04	0.0020	0.034	0.584
0.7375	3.580	1.922	0.0320	0.493	5.99	0.1300	1.466	9.30	0.0008	0.014	0.314
0.6734	3.488	2.44	0.0289	0.450	5.58	0.1146	1.346	9.28			
0.6152	3.392	3.10	0.0262	0.412	5.18						

mobile species (in our case, the only difference arises from the anion, which also determines the absolute value of the maximum conductivity). On the other hand, in ethanol mixtures the concentration at which the conductivity reaches a maximum varies with IL concentration since the size of the ethanol clusters slightly evolves all throughout the ethanol concentration regime. Moreover, the fact that an ethanol network is not formed in the bulk mixtures determines that a much smaller value of conductivity is observed in ethanol–IL mixtures relative to that of their aqueous homologues.

We have also measured the temperature dependence of κ for some IL mixtures from 288.15 to 318.15 K, the data obtained being compiled in Table 4. Thus, in Figure 2 we plot the temperature dependence of ten selected mixtures: Figure 2(a) shows data for six aqueous ones and

Figure 2(b) for the four equimolar mixtures with ethanol, and in all of them the electrical conductivity increases with temperature in a quasi linear trend. As published before, pure ILs present a VTF-like temperature behavior,³³ following the equation

$$\kappa = A \cdot \exp \left[-\frac{B}{(T - T_0)} \right] \quad (1)$$

where A (the ionic conductivity limit), B (related with the activation energy), and T_0 (the Vogel temperature) are fitting parameters. To verify if mixtures follow eq 1, we fit data presented in Table 4 with this expression, finding a good agreement, as observed in Figure 2. So, it seems that the temperature dependence of IL mixtures with solvents follows the VTF equation as pure ILs do. Let us note that the fitting parameter values obtained (not presented) are not very relevant

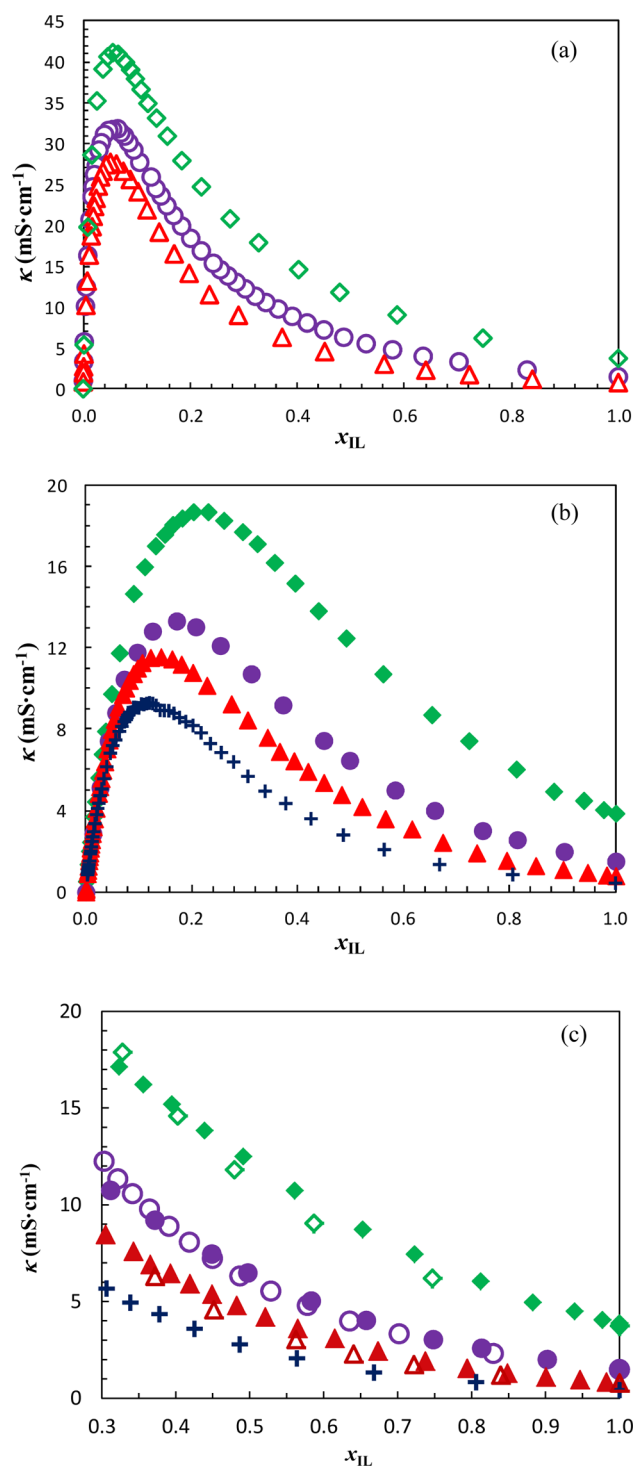


Figure 1. (a) Electrical conductivity of the aqueous mixtures of EMIM-ES (rhombus symbols), EMIM-BS (dot symbols), and EMIM-HS (triangle symbols) against the molar fraction of the IL (x_{IL}) at 298.15 K. (b) Electrical conductivity of the mixtures with ethanol of EMIM-ES (rhombus symbols), EMIM-BS (dot symbols), EMIM-HS (triangle symbols), and EMIM-OS (cross symbols) against the molar fraction of the IL (x_{IL}) at 298.15 K. (c) Electrical conductivity of all mixtures measured with IL molar fraction higher than 0.3. Symbols represent the same systems as in parts (a) and (b) at 298.15 K.

due to the small range of temperature and data points studied in this paper.

As published before by some of us,³⁹ the pseudolattice theory applied to ILs⁴⁰ gives a universal curve without fitting parameters, predicting the normalized electrical conductivity of IL mixtures with polar solvents, which reads

$$\frac{\kappa}{\kappa_{\max}} = \xi_{IL}(2 - \xi_{IL}) \quad (2)$$

where κ_{\max} is the maximum value of the conductivity in each system and ξ_{IL} is the reduced concentration, i.e.

$$\xi_{IL} = \frac{c}{c_{\max}} \quad (3)$$

the IL concentration (in moles per liter) divided by the IL concentration at that maximum conductivity value. Note that eq 2 is a parabolic curve, where at the maximum conductivity $\xi_{IL} = 1$ and $\kappa/\kappa_{\max} = 1$ too. In Figure 3 we plot our experimental data as κ/κ_{\max} vs ξ_{IL} for the aqueous systems (a) and for the ethanol ones (b). For all systems, the normalized data points follow quite well the universal curve given by eq 2, except for IL concentrated mixtures where discrepancies happen, different for each aqueous system but exactly the same for those with ethanol. The obtained curves can be fitted with high accuracy in all ranges of concentrations if we include two additional terms to the universal parabolic eq 2

$$\frac{\kappa}{\kappa_{\max}} = \xi_{IL}(2 - \xi_{IL}) + D^*\xi_{IL}(1 - \xi_{IL})^2 + E^*\xi_{IL}(1 - \xi_{IL})^3 \quad (4)$$

where D^* and E^* are fitting parameters. This eq 4 provides excellent fits for all systems studied, as observed in Figure 3, where we plot the resulting curves. The obtained fitting parameters are given in Table 5 (note that the fitting curve is the same for all systems with ethanol, and it has $D^* = 0$), where we have also included the corresponding standard deviations, s , defined as

$$s = \sqrt{\frac{(Y - Y_{\text{calcd}})^2}{N - 1}} \quad (5)$$

where $Y = \kappa/\kappa_{\max}$; the calcd sub index means data obtained from eq 4; and N is the number of data points for each system.

A possible explanation for the deviations of the experimental data from the universal curve given by eq 2 but fitting the expanded version given by eq 4 goes as follows. As one can see in ref 39, the latter curve rests upon the following assumptions: (i) a structural model in which the bulk mixture is represented by a pseudolattice of independent ionic-like (α) and solvent-like (β) cells and (ii) a linear dependence of the ionic mobility on the ionic concentration, which is in turn equivalent to concentration-independent ionic jumping frequencies. The first assumption assumes that IL–solvent interactions are negligible, and the latter assumption implies that the jumping frequencies are not affected by the nature of cells in the neighborhood of a given ion. Of course, both assumptions break down in highly concentrated mixtures, which are known to exhibit a rich variety of nanoscopic morphologies in the different concentration regimes associated to complex ion–ion, ion–solvent, and solvent–solvent interactions, determining the existence of deviations from the universal curve. As a first approximation to the problem, we simply consider in this work the influence of interactions of an ion in a cell with its nearest-neighbor cells in the jumping frequencies. At the lowest order, one can then

Table 4. Electrical Conductivity of Selected Aqueous Mixtures, and for Equimolar Mixtures with Ethanol, of the Studied IL at Four Temperatures

IL	solvent	x_{IL}	κ (mS/cm)			
			288.15 K	298.15 K	308.15 K	318.15 K
EMIM-BS	water	0.50	3.92	5.91	8.39	11.4
EMIM-BS	water	0.30	8.41	12.1	16.5	21.7
EMIM-BS	water	0.10	20.8	28.4	36.9	46.5
EMIM-HS	water	0.50	2.33	3.57	5.16	7.12
EMIM-HS	water	0.30	5.60	8.15	11.3	15.0
EMIM-HS	water	0.10	17.3	23.4	30.15	37.8
EMIM-ES	ethanol	0.50	9.151	12.15	15.7	19.6
EMIM-BS	ethanol	0.50	4.67	6.47	8.58	11.0
EMIM-HS	ethanol	0.50	2.62	3.96	5.17	6.83
EMIM-OS	ethanol	0.50	1.66	2.44	3.43	4.62

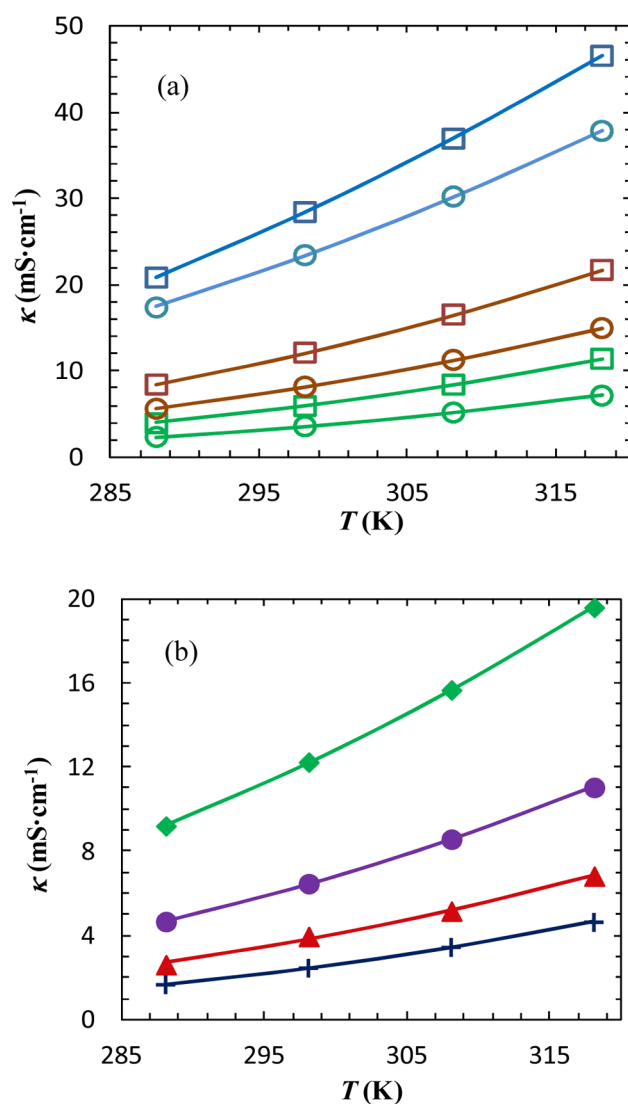


Figure 2. (a) Temperature dependence of selected aqueous mixtures of ILs. Square symbols represent mixtures with EMIM-BS and IL molar fraction equal to (from bottom to top): $x_{\text{IL}} = 0.50, 0.30$, and 0.10 . Dot symbols are for mixtures with EMIM-HS and IL molar fraction equal to (from bottom to top): $x_{\text{IL}} = 0.50, 0.30$, and 0.10 . Lines are the best fit of a VTF eq 1. (b) Temperature dependence of equimolar mixtures of ILs with ethanol. Rhombus symbols represent mixture with EMIM-ES, dot symbols for that with EMIM-BS, triangle symbols for the mixture with EMIM-HS, and cross symbols for that with EMIM-OS. Lines are the best fit of a VTF eq 1.

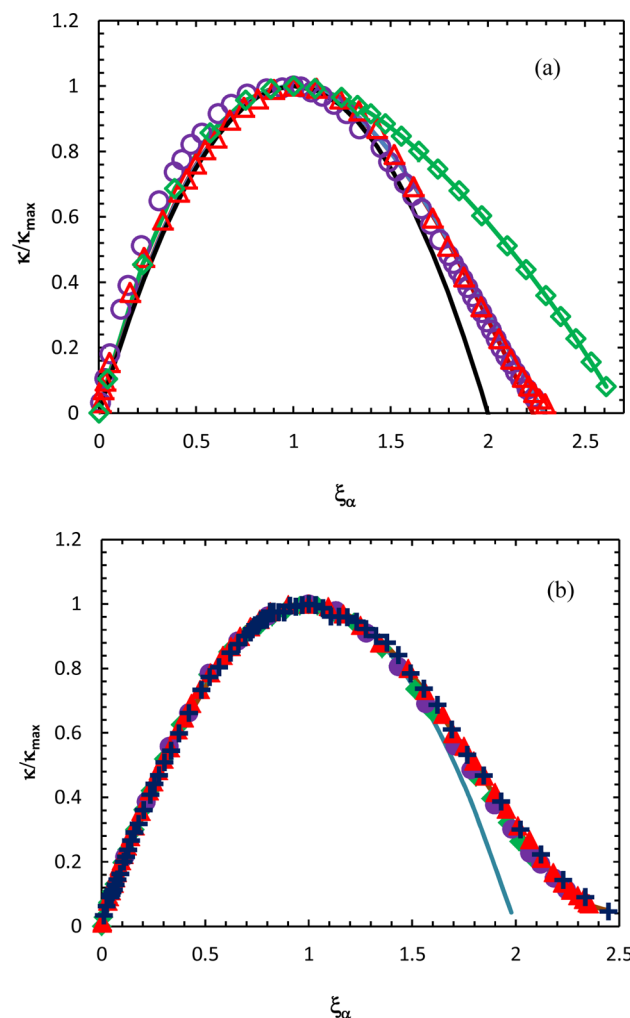


Figure 3. Bahe-Varela universal representation of the normalized electrical conductivity at 298.15 K for (a) aqueous and (b) solutions with ethanol of EMIM-ES (rhombus symbols), EMIM-BS (dot symbols), EMIM-HS (triangle symbols), and EMIM-OS (cross symbols). The lines are the parabolic universal expression given by eq 2 and the expanded version given by eq 4 (lines on the data points).

assume that the jumping frequencies depend on concentration in a linear fashion

$$\nu_{\mu} = \nu_{\mu}^0 + \nu_{\mu}^1 c \quad (6)$$

Table 5. Best Fitting Parameters D^* and E^* of Equation 4 and D_1 to D_4 of Equation 9 to the Data at 298.15 K^a

+ water	EMIM-ES	EMIM-BS	EMIM-HS	
D^*	0.363	0.103	0.089	
E^*	0.072	−0.040	−0.066	
s	0.010	0.049	0.025	
+ ethanol	EMIM-ES	EMIM-BS	EMIM-HS	EMIM-OS
D^*	0.000	0.000	0.000	0.000
E^*	−0.154	−0.154	−0.154	−0.154
s	0.020	0.021	0.019	0.010
+ water	EMIM-ES	EMIM-BS	EMIM-HS	
D_1	61.89	70.10	66.00	
D_2	−18.39	−68.71	−81.153	
D_3	4.193	−5.77	−10.56	
D_4	−10.59	25.36	38.35	
s	0.030	0.431	0.450	
+ ethanol	EMIM-ES	EMIM-BS	EMIM-HS	EMIM-OS
D_1	20.45	9.159	21.04	12.38
D_2	13.64	−19.14	19.44	−7.04
D_3	−1.73	4.77	−2.59	2.83
D_4	4.99	−18.157	7.83	−11.10
s	0.368	0.166	0.408	0.1566

^aStandard deviations for each system, given by eq 5, are included.

So the ionic mobility is quadratic in ionic concentration, and consequently, the ionic conductivity contains a cubic term in concentration

$$\kappa = Ac + Bc^2 + Dc^3 \quad (7)$$

After some lengthy but otherwise trivial algebra, one can show that the above equation can be reduced to the form given by eq 4, except for the third term on the right-hand side. A complete theoretical justification of that expanded equation is now in progress.

Finally, from the data of the specific electrical conductivity, κ , we extract the molar electrical conductivity, Λ_m , following the usual equation⁴¹

$$\Lambda_m = \kappa/c \quad (8)$$

with κ and c given in Tables 2 and 3. The resulting data are plotted vs concentration in Figure 4(a) for aqueous systems and Figure 4(b) for those with ethanol. Obviously, molar conductivity is much higher for solutions with water than for those with ethanol for diluted mixtures. We have fitted the molar conductivity data to an equation derived from Onsager theory,⁴¹ which was also used by other authors^{10,12,13,15}

$$\Lambda_m = D_1 - D_2\sqrt{c} + D_3 \cdot c \cdot \log c + D_4 \cdot c \quad (9)$$

where D_i are fitting constants. As observed in Figure 4, the resulting curves reproduce the data with high quality. In Table 5 we include the obtained D_i fitting parameter values for the three systems with the corresponding standard deviation. We have used the conventional expressions of the Onsager theory for rationalizing the behavior of the molar electrical conductivity, but this must be considered as a purely phenomenological effort of understanding the actually complex charge transport in these systems. In the case of ethanol mixtures, the absence of an ethanol network³⁷ seems to lead to a linear behavior of the molar electrical conductivity over a wide concentration interval, while the increase of Λ_m in aqueous mixtures with water concentration is much steeper, probably

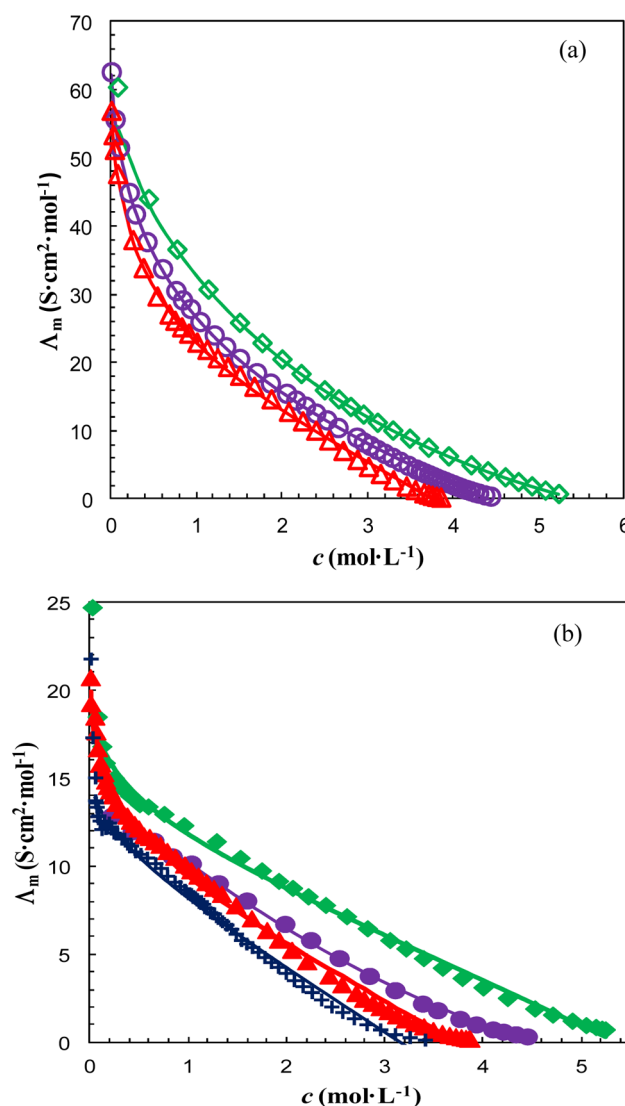


Figure 4. Molar conductivity vs molarity at 298.15 K for solutions with (a) water and (b) ethanol of EMIM-ES (dot symbols), EMIM-BS (square symbols), EMIM-HS (triangle symbols), and EMIM-OS (cross symbols). Lines are the best fit of eq 9 with the parameters given in Table 5.

reflecting the formation of a water network in the bulk. As for the electrical conductivity, a full description of this magnitude demands a detailed understanding of the structural features of the mixture in the different concentration regimes, which include the formation of several nanoscopic structures ranging from micelles in the concentrated IL regime to ionic and polar networks in the diluted solvent regime.

CONCLUSIONS

We measured the electrical conductivity of seven binary systems formed by water or ethanol as solvents with any of the four ionic liquids of the family 1-ethyl-3-methylimidazolium alkyl sulfate (EMIM- C_nS) in all ranges of concentrations at 298.15 K. In addition, ten selected mixtures were measured at four temperatures. Only one of the seven systems studied here had been published before, and those results were compared with ours, which have also been discussed with the electrical conductivity data for other IL mixtures published. A decrease of the conductivity value is observed when the alkyl

chain of the anion increases as expected. For low solvent concentration, the increase of electrical conductivity with addition of solvent was similar for both, but for more diluted mixtures, it is much higher for aqueous systems than for those with ethanol. As previously observed, all systems studied here also present a peak in the electrical conductivity at a given concentration; this is roughly the same for all aqueous systems but moves to more diluted mixtures for the ethanol ones. Temperature behavior of the selected mixtures can be fitted to a VTF-like equation just as happens for pure ILs. We compare our data with the universal curve deduced from the pseudolattice Bahe-Varela model with very good agreement, except for very IL-concentrated mixtures. We have introduced two new phenomenological terms to that equation that provide a very good fit in all ranges of concentrations. We have related the additional terms to concentration-dependent jumping frequencies due to interionic interactions. Moreover, from electrical conductivity data, we calculate molar conductivity obtaining similar curves for all systems, increasing its value with the solvent concentration. However, the shape of the curve depends on the solvent; thus, while for aqueous systems the increase is concave, for the systems with ethanol it is linear for a broad range of concentrations. Finally, we have fitted a theoretical curve inspired in Onsager theory with good agreement.

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Notes

The authors declare no competing financial interest.

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