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Electrochemical, Thermodynamic, and Physical Properties of Tetradecyltrihexylphosphonium ($[P_{6,6,6,14}]^+$) and Methyl-propyl Piperidinium Containing Ionic Liquids and their Propylene Carbonate Solutions

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Abstract

The viscosity, conductivity, electrochemical window and related thermodynamic properties such as excess volume and dynamic viscosity deviation of two phosphonium ionic liquids were measured and calculated for "as-supplied" and dried neat liquids and also v/v mixtures of 99/1, 95/5, 90/10, 75/25, and 50/50 of the ionic liquids with propylene carbonate (PC). Tetradecyltrihexylphosphonium dicyanamide ($[P_{6,6,6,14}]^+$dicyanamide), Cyphos 105, and tetradecyltrihexylphosphonium bistrifluororomethanesulfonimide (called bistriflimide) ($[P_{6,6,6,14}]^+$bistriflimide), Cyphos 109, ionic liquids were studied. Generally speaking, there were slight differences in the measured properties of the wet and dried IL solutions which were reflected in differences if the calculated properties. The measured and calculated properties were compared with those collected and derived from a piperidinium-based ionic liquid, methyl-propyl piperidinium bistriflimide. Arrhenius plots for both the viscosity and conductivity were linear, with the linearity of the Litovitz plots being slightly higher. The viscosity and conductivity of the phosphonium solutions yielded Walden Plots that differed from Walden plots of piperidinium solutions and other ionic liquid solutions. For the phosphonium based ionic liquids, the ionicity was found to increase with increasing dilution in propylene carbonate. The electrochemical windows of the ionic liquids were determined as a function of the concentration of the ionic liquid present in the solution. The size of the window generally initially decreased and then increased with the addition of PC for the $[P_{6,6,6,14}]^+$dicyanamide ionic liquid increasing from 3.4 V in the 95/5 v/v (volume Cyphos 105) to volume of PC solvent) to 3.7 in the 50/50 dried IL case. The electrochemical windows of the dried liquids were slightly larger 3.5 V for the 95/5 v/v and 4.2 V for the 50/50 v/v Cyphos 105/PC solutions. The electrochemical window was larger and the conductivity was higher for the piperidinium IL solutions, but since the ionicity increases with dilution, the phosphonium based IL solutions may prove favorable for processes such as electrochemical reduction.

Introduction

Ionic liquids, (ILs), have unique electrochemical and thermodynamic properties,[1-5] and they have been touted as a medium for electrochemical reduction and deposition of a variety of metals from solution.[6-8] Liquids with an imidazolium, a pyridinium, or pyrrolidinium cation have shown some ability to support reduction of metals with a low standard reduction potentials as in the case of the rare earth metals.[9] Currently molten salts are often used for the electrochemical

reduction of rare earth metals at temperatures in excess of 300 ºC.[10] A suitable ionic medium present in the liquid state at room or near-room temperatures would represent a significant savings in the energy requirement associated with the electrochemical reduction and refinement of these metals. Additionally, the viscosity and conductivity of the candidate neat ionic liquids and their solutions in an appropriate solvent, are also important synergistic properties that deserve consideration in the search for an efficient electrochemical reduction medium. Highly viscous ionic liquids with poor conductivity require significantly more energy for the reduction of rare earth metal ions in solution.

ILs have also been studied as a main component for the preparation of electrolyte solutions in batteries and supercapacitors. However, the relatively high viscosity and low conductivity of many pure ionic liquids contribute to limitations in their use for battery, capacitor, and electrochemical reduction applications. As noted by others, combining the ionic liquid and a suitable low-viscosity solvent with a large electrochemical window may provide a suitable medium with lower viscosity and higher conductivity.[11] In the case of battery and capacitor applications, propylene carbonate (PC) has been investigated as a solvent for this purpose.[2]

Past studies have been performed to investigate the changes in viscosity and conductivity for IL-PC solutions for more commonly available ILs such as imidazolium and pyrrolidinium cation-based ILs with tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), bistrifluororomethanesulfonimide, or dicyanamide anions due to the relatively higher ionic conductivities and potential windows associated with these ions.[2] Phosphonium cation based ionic liquids have some good qualities for these purposes. as well. They have relatively higher thermal and electrochemical stability and offer several advantages over other types of ILs. These ILs are found to have better solubility of organic and inorganic solutes, including super-critical carbon dioxide. They also possess reasonable ionic conductivity and good solvation power even though these ILs are either nonpolar or less polar than other ILs.

However, relatively little data has been collected for phosphonium based ionic liquid mixtures with a solvent like propylene carbonate, (PC), and these studies will add to the database and provide needed information on the potential use of the phosphonium-based ILs for capacitor and battery applications. In addition, the *interaction differences* associated with the various types of ionic liquids have been noted, and also of the ILs with various solvents.[11-16] These studies will further the interpretation of the differences by comparing phosphonium ILs to a piperidinium ionic liquid.

For both electrochemical reduction/refinement purposes and for battery/capacitor applications, the type and strength of the intermolecular interaction and the effect of the solvent on that interaction will be important. Ionic liquids based on a phosphonium cation have been shown to have significantly different intermolecular interactions than imidazolium or pyrrolidinium based ionic liquids. The intermolecular interactions in the latter ionic liquids support a larger mesostructured interaction, whereas ionic liquids with a phosphonium cation are suspected to have more of an ion-pair type interaction in many cases.[17,18] Molecular dynamics calculations by the Canongia Lopes group have shown that different mesoscopic bi-continuous nanostructures are realized with several different cation geometries.[19] These bi-continuous structures are thought to be anion and cation layers in nitrogen- based ILs with a cation-anion

pairs like imidazolium and trialkylmethylammonium bistriflimide. However, calculations suggest that these bi-continuous structures may not exist with tetraalkylphosphonium bistriflimide.[19] They found that the volume ratio of uncharged to charged groups (V_{alkyl}:V_{polar}) and the relative position of the alkyl groups on the cation greatly affected the formation of mesoscopic layering. In the imidazolium and trialkylmethylammonium IL's a larger V_{alky}:V_{polar} ratio makes the cation larger and more amphiphilic, but in largely symmetric tetraalkylphosphonium-bistriflimide ILs an increasing V_{alkyl}:V_{polar} makes the cation larger but not more amphiphilic. The results inferred the anions are more likely to be paired with a single cation creating an ion pair,[19] and if meso-structures are present, they are likely weak thread-like network structures with the anions between the alkyl chain threads. These differences may cause significant variations in the physical properties of both the neat liquids and in solutions of ILs with similar anions but with different cations.

Physical properties like the viscosity and the conductivity should be good indicators of the degree of interaction between the constituents in the solution. The addition of a solvent will cause some interruptions in larger meso-structures like bi-continuous layers of cations and anions. Bi-continuous layered types of mesoscopic structure likely move current within the anionic and cationic layers much like electron and holes in a metal leading to a high conductivity relative to ILs without a bi-continuous layer. Ionic liquids with ion pair and weak threaded network type interactions will have lower conductivity. As stated above, more ion pair and threaded type interactions are suspected for tetraalkylphosphonium ILs.

Addition of a solvent like propylene carbonate should affect the conduction of ions differently for ILs with meso bilayer interactions as opposed to those with more ion pair interactions. Conduction of charge for meso bilayer type interactions would be slippage of the larger charged bilayers past one another whereas with an ion-pair structure, the ion pairs would have to break apart and then move past one another and through solvent and other ion pairs. Based on these interactions, changes in the conductivity should be closely linked with changes in the viscosity for a bi-layer meso-structured liquid. Viscous flow is the slippage of layers of fluid past each other, and changes in the intermolecular interactions would affect viscosity and conductivity at the same time. Thus, the activation energies for momentum transfer and conduction would reflect these differences and change roughly equally for a meso bilayer structured liquid. Also, the ionicity of a solution of these types of ILs may decrease slightly with dilution due to a disruption of the conductive layers. Conversely, conduction of charge for an IL with ion pair structure would be governed by the strength of the ionic interaction energy and the intermolecular forces in the liquid. Here changes to the conductivity would likely be more difficult requiring more activation energy due to the strength of the ion pair interaction. Also, as the solvent breaks up the ion pairs, the ionicity of the solution should instead increase with dilution. The ionicity change differences between meso-bilayer structured interactions and ion pair interactions would be reflected in the Walden plots.

The electrochemical window of the mesostructured solutions should be more altered as the concentration of the solvent increases. The presence of meso-structure in an ionic liquid would likely be more disrupted by the solvent, as the ion-pair type interactions should persist to higher degrees of dilution due to the stronger intermolecular interactions. The presence of water is also likely to influence these interactions as it could assist in breaking up the ion pairs.

In this study the viscosity and conductivity of two commercially available phosphonium ionic liquids Cyphos 105, (tetradecyltrihexylphosphonium dicyanamide or ($[P_{6,6,6,14}]^+$dicyanamide) and Cyphos 109, (tetradecyltrihexylphosphonium bistriflimide or ($[P_{6,6,6,14}]^+$bistriflimide) were measured along with those of a piperidinium-based ionic liquid, methyl-propyl piperidinium bistriflimide (MPPipTf2N). The water content of ionic liquids has been shown to affect the mobility of the ions in the solution, and these studies were completed both with Cyphos 105 and Cyphos 109 ionic liquids with water content "as-supplied" (1200 ppm and 600 ppm water) and also after drying the liquids to a water content below 60 ppm. The water content of the as-supplied MPPipTf2N IL was already low at 60 ppm. These ionic liquids were also diluted with PC resulting in solutions of 99:1, 95:5, 90:10, 75:25, and 50:50 volume ratio. The corresponding mole fractions were approximately 0.93, 0.71, 0.52, 0.27, and 0.11 for the Cyphos solutions, and 0.96, 0.84, 0.71, 0.45, and 0.21 for the MPPipTf2N solution). The viscosities, conductivities, and related kinetic and thermodynamic properties of these solutions were determined at several temperatures. The electrochemical window of the dried pure ionic liquids and their solutions in PC were determined at room temperature, 295K.

Experimental

The Cyphos 105 and Cyphos 109 ionic liquids (ILs) were obtained from Solvay and the MPPipTf2N was obtained from IoLiTec (Ionic Liquids Technologies GmbH, Heilbronn, Deutschland). For the "as-supplied" experiments, the ionic liquids were used directly from their container without further purification or filtering. The water content of the Cyphos ionic liquids were measured by Karl Fischer titration and found to contain 1200 and 600 ppm water respectively for Cyphos 105 and Cyphos 109 and 60 ppm water for MPPipTf2N. For the "dried Cyphos experiments, the ionic liquids were first dried by raising the temperature of the liquids to about 95 ºC under vacuum. The water content of these liquids was determined to be 17 and 32 ppm for the Cyphos 105 and Cyphos 109 respectively. These liquids were then taken into a dry, low-oxygen glovebox for solution preparation. The anhydrous propylene carbonate, (PC, 1,2-Propanediol cyclic carbonate, 4-Methyl-1,3-dioxolan-2-one), CAS # 108-32-7 and purity 99.7%, was received in a septum-capped bottle from Sigma-Aldrich and required no further treatment. The 99/1 (volume/volume, v/v) solutions were made using the following procedure. For the 99:1 solution, a pipetting tool was used to pipette 9.90 mL of the ionic liquid (IL) of interest into a dry weighed sample vial. The weight of the vial and IL were then recorded. A separate pipette was use to add 0.10 mL of dry PC to the same vial and then the total weight was recorded. The contents were then stirred for several minutes resulting in a homogenous solution of IL and PC. A similar procedure using the appropriate volume of each liquid was used to create the other solutions resulting in 99:1, 95:1, 90/10, 75:25, and 50:50 v/v mixtures of "as-supplied" and dried Cyphos 105/PC, Cyphos 109/PC, and dried MPPipTf2N in PC. These solutions were used to make each of the required physical property measurements. The mole fractions of the solutions determined from the volume and densities of the IL and PC were in good agreement with the mole fraction of the solutions determined from the mass measurements (See Table 1). Note that the mole fractions calculated by both methods are in reasonable agreement with each other. After the solutions were prepared, they were carefully examined for any evidence of phase separation. No phase separation was found in any of the IL/PC solutions prepared for these studies.

Table 1. Mole fractions of the 50/50, 75/25, 90/10, 95/5, and 99/1 v/v Cyphos Solutions Determined from the volume and the density, and directly from the measured masses.

Cyphos 105					
T(K)	**50/50**	**75/25**	**90/10**	**95/5**	**99/1**
298	0.138	0.310	0.562	0.728	0.932
Mass Calc.	0.125	0.294	0.552	0.719	0.937
Cyphos 109					
298	0.112	0.268	0.518	0.693	0.921
Mass Calc.	0.102	0.261	0.515	0.691	0.940

The viscometer used to measure the dynamic viscosity was a Cambridge Applied Scientific Oscillating Piston Viscometer with a model VL-4100 controller. The pistons available for these measurements were in the 0.2-10, 10-200 and 100-2000 cP ranges. Before measuring the viscosity of the samples, the viscosity of a standard sample, Fluid 100 from Brookfield Engineering Laboratories Inc. was measured to ensure the viscometer was operating within specifications. During the evaluation of the viscosity of the solutions of the ionic liquids in PC, the piston had to be changed due to the large change in the solution viscosities upon dilution. Measurements were made in the overlapping region, one with the higher viscosity piston, and one with the lower viscosity piston to evaluate consistency. The readings were typically within 5% of each other.

The conductivity meter was an EC Meter Model CM-30R from DKK-TOA Corporation. The conductivity cell used to make the measurements was a Type CT-157101B with cell constant 97.9. The conductivity measurements were made at the same time as the viscosity measurements. A test tube containing the conductivity cell was immersed in the same water bath that controlled the temperature of the viscometer, a Cole Parmer Polystat water bath. The water bath temperature reading was within 0.2 ^{o}C of the on-board thermocouple measurements from the viscometer, and differed just slightly more (no more than 0.6 ^{o}C) from the in-probe thermocouple on the conductivity meter.

It proved somewhat difficult to collect the data exactly at the desired temperatures. The data collected with both the viscometer and the conductivity probe are viscosity and conductivity values where the temperature readings were within 5% of the target temperatures. In general, the uncertainties mentioned for measured values are relative standard deviations, and the uncertainties in calculated values were determined through propagation of error using the described uncertainties in the physical measurements.

The density (D) measurements were made on each neat liquid and solution with a Mettler Toledo Model DM40 densitometer. The density information was used to calculate the mole fraction and also the molarity of the solutions using Equation 1.:

$$M(soln) = D(soln) * \frac{V(IL \text{ in soln}) * D(IL) / Mm(IL)}{(V(PC \text{ in soln}) * D(PC) + V(IL \text{in soln}) * D(\text{pure IL})} \quad (1)$$

where D is the density, V is the volume, and Mm is the molar mass. For the density measurements, the temperature of each measurement was controlled to within 0.2 ^{o}C.

The electrochemical data was obtained using a Gamry Model PC4/750 electrochemical station. The working electrode was a glassy carbon electrode of area 0.071 cm^2. It was polished and rinsed with acetone and methanol before use. The counter electrode was a 0.2 mm diameter platinum wire coiled into ~5 loops of 0.5 mm diameter, and the reference electrode consisted of a single 0.2 mm diameter platinum wire. The scan rate used was 0.20 V/s.

Results

Experimentally Measured Solution Properties

Measurement and tabulation of the values of the solution densities provides the necessary information for calculation of the concentration in terms of the molarity and also mole fraction of the solution. These concentration units are used in the typical calculations and plots of physical properties and derived thermodynamic properties. Representative measured densities of dried (dry) and "out-of-the-bottle" (wet), for Cyphos 105 are provided in Table 2. The measured densities for all these Cyphos 105, Cyphos 109, and MPPipTf2N solutions are provided in Tables 1a-c in the Supplemental Information section. Representative calculated mole fractions and molarities of the solutions are provided in Table 3 for Cyphos 105, and for all solutions in Table 2a-c in the Supplemental Information section. Note that the differences in the densities are small and many within the experimental uncertainties of $^{+}/_{-}$ 0.002 g/ml for these measurements.

Table 2. Densities (in g/mL) of the Cyphos 105/PC solutions as a function of temperature concentration, and water content.

Temp K	50/50 soln.	75/25 soln.	90/10 soln	95/5 soln.	99/1 soln.	Cyphos 105
1200 ppm H_2O						
293	1.048	0.975	0.932	0.914	0.902	0.899
313	1.028	0.957	0.916	0.898	0.886	0.883
333	1.008	0.940	0.899	0.882	0.871	0.868
17 ppm H_2O						
293	1.045	0.973	0.929	0.914	0.902	0.899
313	1.026	0.955	0.912	0.898	0.887	0.884
333	1.006	0.937	0.896	0.882	0.871	0.868

Table 3. Concentration of the Solutions in terms of the volume ratio, molarity, and mole fraction. Values given are at 293 K.

Volume Ratio V_{IL}/V_{PC} Soln. Conc.	Wet Solution Molarity mol(IL)/L(soln)	Dry Solution Molarity mol(IL)/L(soln)	Mole Fraction Wet Ionic Liquid	Mole Fraction Dry Ionic Liquid
50/50	0.747	0.811	0.121	0.125
75/25	1.17	1.22	0.293	0.295
90/10	1.44	1.47	0.555	0.552
95/5	1.53	1.55	0.724	0.719
99/1	1.61	1.62	0.932	0.937
Pure 105	1.63	1.63	1.00	1.00

Note that the values given in Table 3 were at 293 K and the values of the concentration differ slightly at other temperatures.

The values of the mole fraction can be combined with the experimental values of the viscosities and conductivities to calculate several thermodynamic properties related to the interactions in the liquids including the excess volume, deviations from ideality in the dynamic viscosity, and the fluidity. The viscosities of the "as-supplied" (wet) and dried (dry) solutions measured as a function of temperature and dilution in PC for Cyphos 105 and Cyphos 109 are given in Table 4a-b. Viscosity data for all of the IL solutions studied is provided in Tables 3a-c in the Supplemental Information section. The uncertainty in the individual viscosity measurements was less than 1%, but an uncertainty of 5% is a better estimate due to the uncertainty in the temperature measurements. In almost all cases the viscosity of the dried solutions is higher than the viscosity of the wet solutions, and the difference is greater than 5% of the higher value. However, for Cyphos 109 solutions, the viscosity of the dried solutions was often lower than for the wet solutions, especially for lower 109 mole fractions and lower temperatures. Here the differences were often larger than 5%. The wet Cyphos 105 solutions have a much higher water content, twice that of the Cyphos 109 solutions. This could be the source of the difference in the viscosity behavior of the wet and dry solutions. The anions are also different and the smaller anion of Cyphos 105 may have stronger intermolecular interactions with water in the solns. Note that the literature values of the viscosity for pure PC range from 2.73 mPa s at 293 K to 1.37 mPa s at 333 K.[11]

Table 4a. Solution viscosity (in mPa s) as a function of temperature and concentration for Cyphos 105 in PC.

Temp K	50/50 wet	dry	75/25 wet	dry	90/10 wet	dry	95/5 wet	dry	99/1 wet	dry	Pure wet	dry
293	13.5	13.6	41.3	45.3	119	129	212	223	363	386	413	461
298	11.2	11.5	34.0	35.9	89.9	104	165	172	273	306	323	352
303	9.51	10.1	28.1	30.1	69.7	82.1	128	132	208	235	247	264
308	8.39	8.24	23.4	25.0	56.2	66.2	101	106	162	183	192	205
313	7.63	7.16	19.7	21.2	47.6	54.4	81.1	83.5	130	142	152	161
333	4.61	4.50	11.2	11.7	24.0	27.2	38.6	40.1	57.3	60.5	67.9	66.5

Table 4b. Solution viscosity (in mPa s) as a function of temperature and concentration for Cyphos 109 in PC.

Temp K	50/50 wet	dry	75/25 wet	dry	90/10 wet	dry	95/5 wet	dry	99/1 wet	dry	Pure wet	dry
293	13.4	11.5	39.5	39.3	130	118	209	207	352	366	378	413
298	11.0	8.80	32.4	32.1	96.7	91.9	160	158	265	273	300	302
303	9.23	7.91	26.8	27.6	72.9	75.0	124	121	202	215	230	235
308	7.89	6.94	22.4	22.8	56.7	61.2	97.5	96.6	158	166	186	188
313	6.89	6.14	19.0	19.0	46.1	48.8	79.3	77.3	128	130	142	144
333	4.24	3.86	10.6	10.2	23.5	24.7	37.7	36.9	56.1	57.1	63.7	60.9

Derived Kinetic Parameters

In an ideal solution, the interaction energies of the solvent-solvent, the solute-solute, and the solute-solvent would be nearly equal, and for a binary solution of ionic liquid (IL) and propylene carbonate (PC) this would lead to an ideal relationship in the viscosity $\eta = x_{IL}\,\eta_{IL} + x_{PC}\,\eta_{PC}$. Another useful property often defined as a measure of fluid mobility is the fluidity ($F = 1/\eta$), and often the fluidity of a solution is related to the mole fractions by $F = x_{IL}\,F_{IL} + x_{PC}\,F_{PC}$. Representative plots of the viscosity as a function of the mole fraction for the Cyphos 105 ionic wet and dry liquids at several different temperatures is given in Figure 1. In addition, a plot of the Fluidity as a function of the mole fraction for the Cyphos wet and dry ionic liquids and the MPPipTf2N solns. are given in the Supplemental Information Section in Figures 2a-c. Note that based on the ideal relationships $\eta = x_{IL}(\eta_{IL} - \eta_{PC}) + \eta_{PC}$ and $F = x_{IL}(F_{IL} - F_{PC}) + F_{PC}$ and there should be a linear relationship between η and x_{IL} and F and x_{IL}. As the figures show, the relationship is very non-linear for Cyphos 105. The plot shows the viscosity dried (dry) IL solutions are slightly larger than that of the wet IL solutions and the fluidity has the opposite trend. Similar plots for Cyphos 109 and MPPipTf2N solutions in PC are provided in Figures 1a-c and 2a-c in the Supplemental Information Section. As noted previously, for the Cyphos 109 solutions, many show the viscosity of the dry solutions to be lower than for the wet solutions but the difference is small. All are non-linear, although the Cyphos 109 plots appear to be the most linear. In the MPPipTf2N plot there is a noticeable deviation from the Cyphos curve trends at the 99/1 solution concentration.

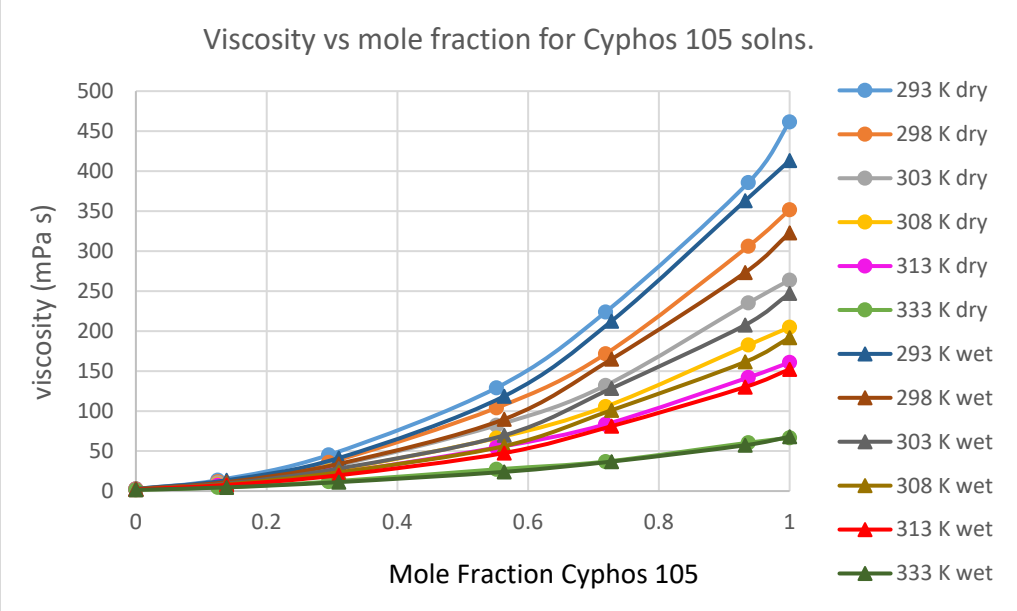
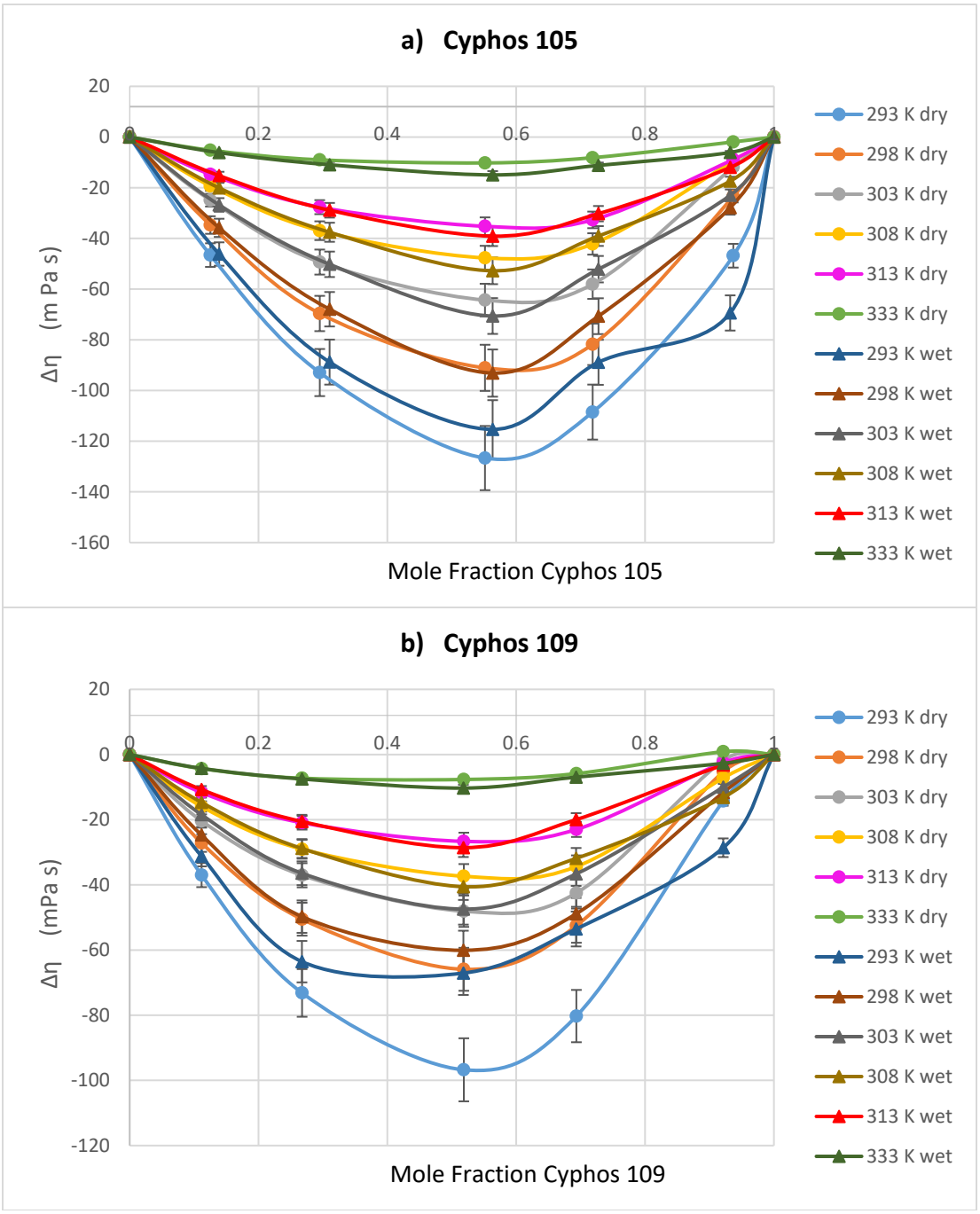
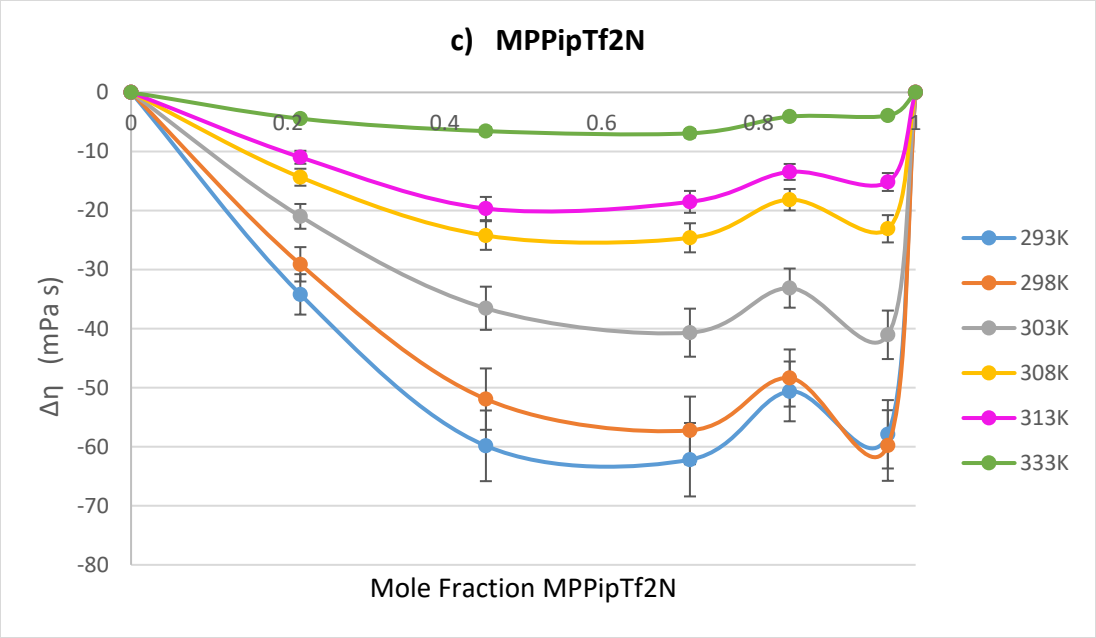


Figure 1. Plot of the viscosity as a function of mole fraction for both wet and dried Cyphos 105 solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

An alternative way often used to show the deviation from ideality is to plot $\Delta\eta = \eta_{actual} - \eta_{ideal}$ as a function of temperature. The $\Delta\eta$ vs mole fraction ionic liquid plots are given in Figures 2a-c. A negative value of $\Delta\eta$ means that the ideal value of the viscosity of the mixture is

larger than the actual viscosity. Thus, the attractive interaction of the fluid layers in the IL-PC soln. is less than the ideal case suggesting the solute-solvent (IL-PC) attractive forces are lower than the IL-IL and PC-PC forces. This result would be consistent with the increase in excess volume for the mixtures if the packing in the mixtures is looser and less organized. Generally speaking, at low mole fractions and lower temperatures, especially for Cyphos 105, the Δη is more negative for the dry solutions, but as the temperature increases the Δη becomes more negative for the wet solutions. However, these small differences are not significant compared to the experimental error in Δη of $^{+}$/- 10%. Note the larger deviations between and wet and dry solns. in the pattern in the 95/5 and 99/1 v/v IL solutions.

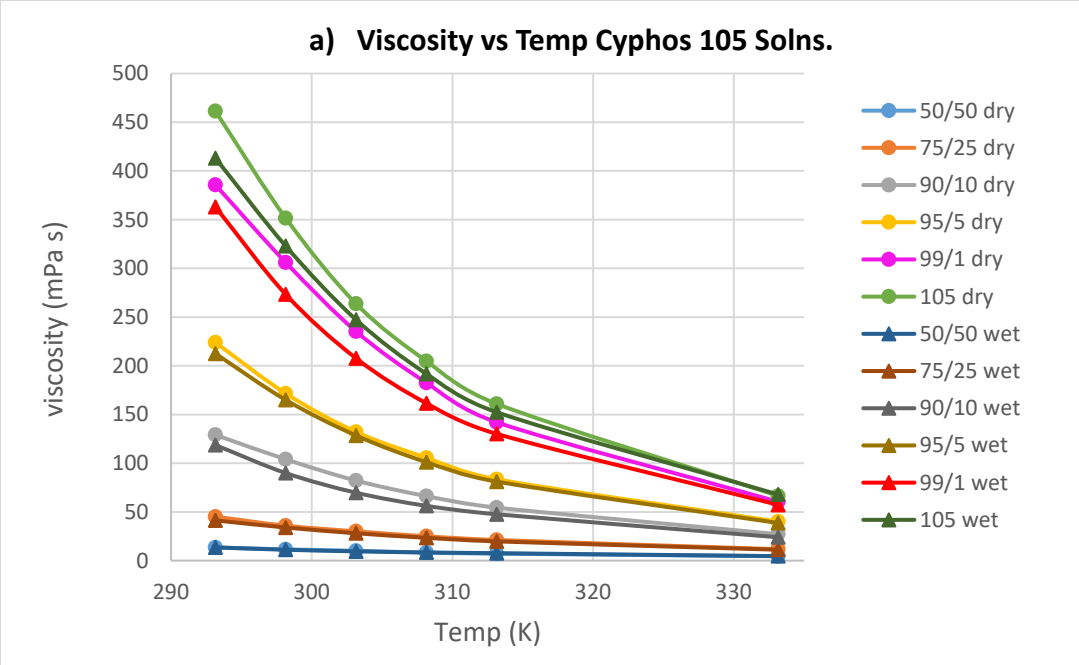


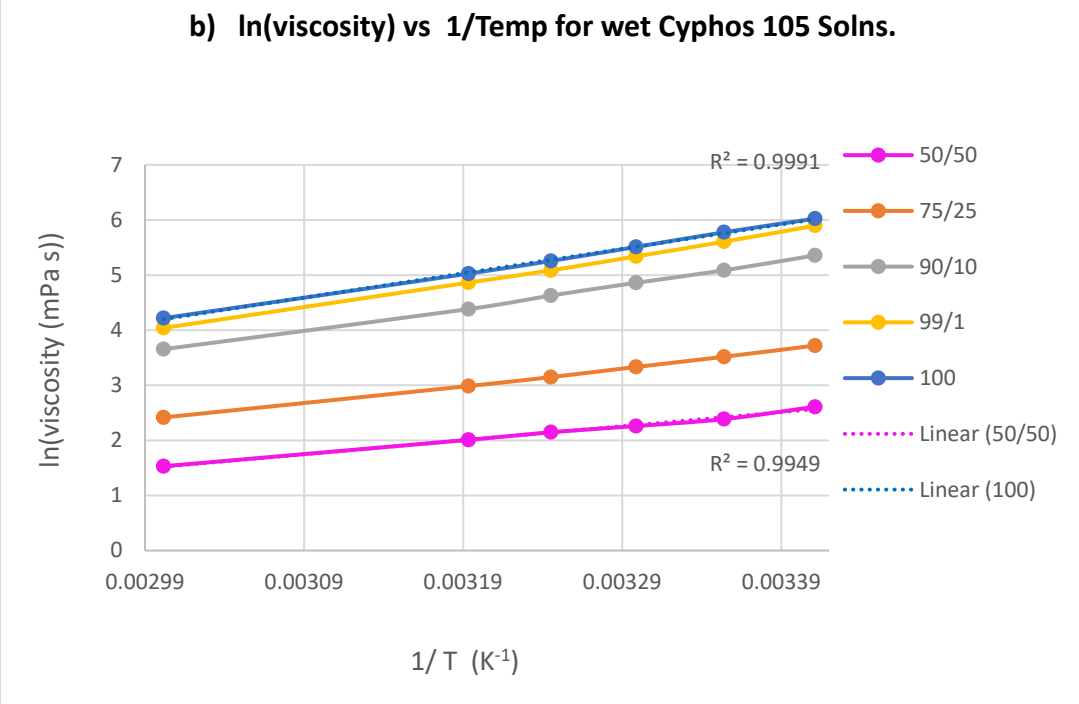


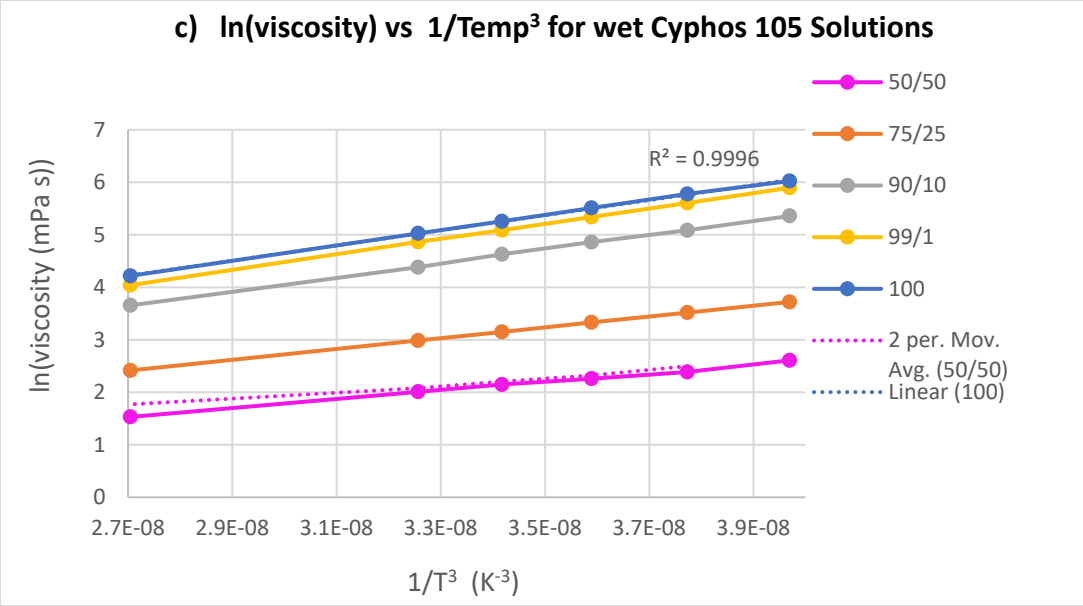
Figures 2a-c. Plots of the deviation from ideality of the viscosity for a) wet and dry Cyphos 105 and b) Cyphos 109 solns in PC, and for c) MPPipTf2N solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

Additionally, the information on the viscosity of the solutions as a function of temperature provides for calculation of the energies of interaction within the ionic liquid from a fairly direct calculation of the activation energies. For base-level, minimal interactions, both the viscosity and conductivity follow Arrhenius like behavior $\eta = A_n \exp[-E_n/RT]$ and $\sigma = A_o \exp[-E_o/RT]$. For stronger interactions, the Litovitz equation is more applicable, $\eta = A'_n \exp[-B_n/RT^3]$, with a similar expression for the conductivity. Here a plot of ln η vs $1/T^3$ which is very linear would be indicative of this type of interaction. If the interaction is even stronger, and more glass-like, then the VFT expression is applicable. These activation energies E_n and E_o correspond to the energy required to move one layer of fluid past another or to conduct ions through the solution. The strength of the interactions definitely affects the ability of current to move in an electrochemical cell and likely plays a role in determining the size of the electrochemical window due to the extra potential associated with moving the ions in solution.

Plots of the viscosity vs temperature were made for wet and dry Cyphos 105 and 109 solns., and for the MPPiPTf2N solns. The plot for wet and dry solns. of Cyphos 105 is given below as part of Figure 3, and all are provided in Figure 3a-c in the Supplemental Information. The Arrhenius plots of the natural logarithm of the viscosity (mPa s) vs 1/temperature were somewhat linear but the Litovitz plots of the natural log of the viscosity vs $1/T^3$ were slightly more linear with values of R^2, for both the pure ionic liquids and also their solutions in PC, greater than 0.996. Representative plots for Cyphos 105 are given in Figures 3a-c. Note the correlation coefficient for the Litovitz plot was slightly closer to 1.


a) Viscosity vs Temp Cyphos 105 Solns.
viscosity (mPa s)
Temp (K)
500
450
400
350
300
250
200
150
100
50
0
290
300
310
320
330
50/50 dry
75/25 dry
90/10 dry
95/5 dry
99/1 dry
105 dry
50/50 wet
75/25 wet
90/10 wet
95/5 wet
99/1 wet
105 wet


b) ln(viscosity) vs 1/Temp for wet Cyphos 105 Solns.
ln(viscosity (mPa s))
1/ T (K-1)
R² = 0.9991
R² = 0.9949
7
6
5
4
3
2
1
0
0.00299
0.00309
0.00319
0.00329
0.00339
50/50
75/25
90/10
99/1
100
Linear (50/50)
Linear (100)



Figures 3a-c. Representative plots of a) the viscosity vs temp., b) ln(viscosity) vs 1/T Arrhenius Plot, and c) ln viscosity vs $1/T^3$ Litovitz Plot for Cyphos 105 solution.

The energies and pre-exponential factors derived for Cyphos 105 from these plots are tabulated in Table 5. The energies and pre-exponential factors for all solutions are given in Tables 4a-c in the Supplemental Information section. Positive values of the energies are related to the amount of energy required for the molecules to move past one another thereby providing flow. The presence and size of the activation energy is associated with the flow of layers of the ionic liquid mixtures in PC and indicates the presence of significant interaction energy when the molecules "squeeze by one another". If the interaction energy is not the same between the solute and solvent molecules then the solution deviates from ideality. The pre-exponential factors are related to the number of collisions encountered and therefore the diffusion rate of the molecules in the liquid.

Table 5. Energies of Activation and Pre-exponential Factors Derived from *viscosity* data fitted to the Arrhenius and Litovitz eqns. for the Cyphos 105 wet and dry solutions in PC.

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**Wet**	**dry**
50/50	21.3	22.7	6.93e5	7.37e5	2.07e-3	1.22e-3	4.89e-1	4.06e-1
75/25	26.5	27.1	8.65e5	8.81e5	7.68e-4	6.52e-4	6.80e-1	6.72e-1
90/10	32.0	31.7	1.04e6	1.03e6	2.24e-4	2.81e-4	8.03e-1	9.56e-1
95/5	34.6	34.9	1.12e6	1.13e6	1.40e-4	1.33e-4	9.95e-1	1.00e0
99/1	37.3	38.0	1.21e6	1.23e6	7.93e-5	6.71e-5	1.12e0	1.13e0
Cyphos105	36.8	40.4	1.20e6	1.28e6	1.12e-4	2.88e-5	1.40e0	1.06e0

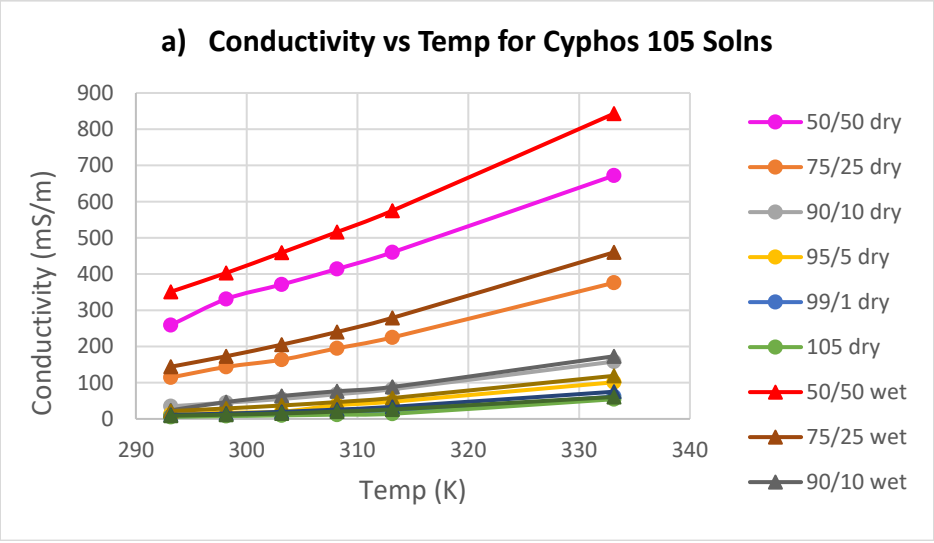
The conductivities (in mS/m) of the solutions were also measured as a function of temperature and dilution in PC. The conductivities for the wet and dry Cyphos 105 solutions are given in Table 6. Note that in most all cases, the conductivities of the wet solutions were higher

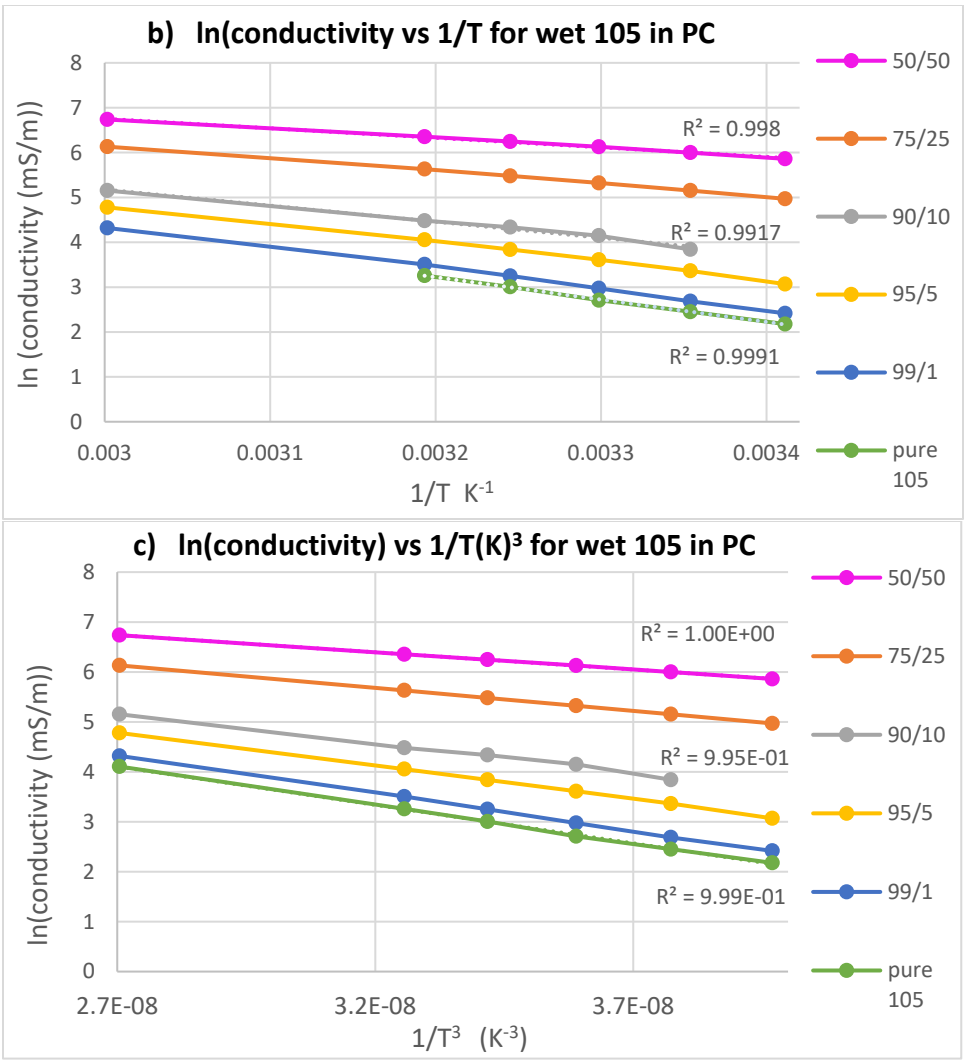
than the conductivities of the dry solutions. Based on a 5% uncertainty in these measurements due largely to the uncertainty in the temperature measures, the differences between the wet and dry solutions are significant. This difference was also observed in the case of the Cyphos 109 solutions with only two exceptions. The conductivity values for all binary solutions of Cyphos 105 IL, Cyphos 109 IL, and MPPipTf2N in PC are provided in Tables 5a-c in the Supplemental Information section.

Table 6. Solution conductivity (in mS/m) as a function of temperature and concentration for Cyphos 105 wet and dry solns. in PC.

Temp K	50/50 wet	dried	75/25 wet	dried	90/10 wet	dried	95/5 wet	dried	99/1 wet	dried	Pure wet	dried
293	351	259	144	114	23.7	34.8	21.5	12.3	11.2	6.5	8.8	5.6
298	403	331	173	144	46.6	44.8	28.9	17.1	14.7	9.3	11.6	7.8
303	459	371	205	163	63.3	55	37.0	20.1	19.6	11.4	15.0	9.7
308	516	414	240	195	76.4	68.2	46.5	37.8	25.8	13.9	20.2	11.8
313	575	460	279	225	88.3	81.8	57.6	47.5	33.3	16.6	26.0	14.2
333	843	672	460	376	173	158	119	101	75.1	62.0	60.7	54.4

As was found for the viscosity data, plots of the conductivity vs temperature were also not linear but the Arrhenius plot and the Litovitz plots showed good linearity as can be seen in Figures 4a-c for Cyphos 105 and solutions of Cyphos 105 in PC. Conductivity vs temperature plots are provided for all solutions in Figures 4a-c in the Supplemental Information section. It is obvious in these plots that the conductivity of the wet solns. for both Cyphos 105 and Cyphos 109 were almost always larger than that of the dried solns. This difference was significant and outside the uncertainties especially for the high temp. – low concentration solns. Similar trends were observed for Cyphos 109 and MPPipTf2N and their PC solutions. The values of the activation energy for conduction were determined from the Arrhenius plots of ln(conductivity) vs 1/T. The Litovitz parameters were also determined from their corresponding plots as well (i.e. ln(conductivity) vs $1/T^3$) where the conductivity is in mS/cm. The values are provided in Table 7 for Cyphos 105 solns., and in Tables 6a-c in the Supplemental Information for all the IL solns. studied.





Figures 4a-c. Cyphos 105 representative plots of a) the conductivity vs temp., b) ln(conductivity) vs 1/T Arrhenius Plot, and c) ln conductivity vs $1/T^3$ Litovitz Plot. Note that the correlation coefficient in the Litovitz Plots was slightly closer to one.

Table 7. Energies of Activation and Pre-exponential Factors Derived from *conductivity* data fitted to the Arrhenius and Litovitz equations for Cyphos 105 wet and dry solns. in PC

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy (kJ/mol)		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**Wet**	**dry**
50/50	17.7	18.4	5.74e5	5.99e5	5.04e5	5.32e5	5.49e3	4.82e3
75/25	23.5	23.8	7.63e5	7.72e5	2.26e6	2.04e6	5.54e3	4.63e3
90/10	29.9	30.5	9.89e6	9.89e5	8.54e6	9.82e6	5.40e3	3.98e3
95/5	34.4	44.0	1.11e6	1.43e6	3.01e7	8.84e8	4.54e3	1.16e4
99/1	38.8	44.3	1.26e6	1.43e6	9.51e7	4.79e8	4.58e3	5.54e3
Cyphos105	41.5	45.0	1.28e6	1.45e6	2.14e8	5.39e8	3.87e3	5.17e3

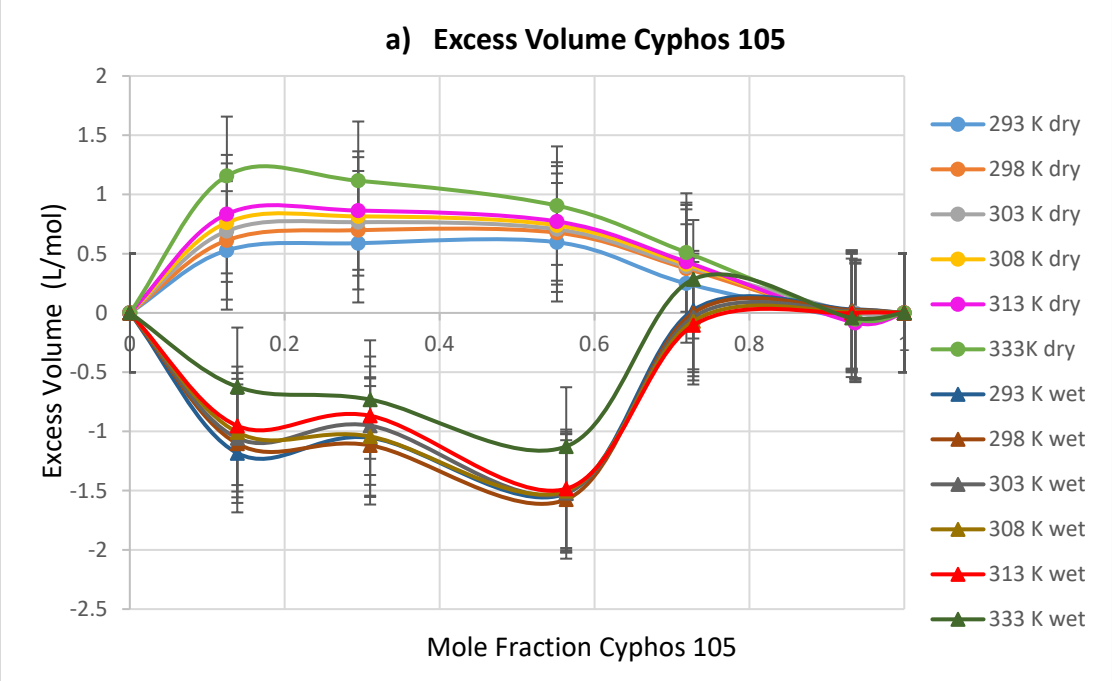
Note that the Activation Energy and Activation Energy Constants are generally higher for the pure ionic liquids based on both the viscosity and conductivity data. Also, the activation energies for the dry solns. are generally slightly larger than for the wet solns. and the change in the activation energy from the 50/50 Cyphos soln. in PC to the neat liquid is larger for the dried ILs. Also, for the Cyphos 105 and 109 IL solutions, the activation energy values decrease by a larger amount, with dilution in PC, for the conductivity data: (45.0 – 18.5 or 26.5) kJ for dry Cyphos 105 and (42.2 – 17.5 or 24.7 kJ) for dry Cyphos 109, than they do for the dry viscosity data: (40 – 22.7) 17.7 kJ 105 and (38.5 – 21.2) 17.3 kJ for 109), suggesting that increases in the conductivity of the ionic solution upon dilution are caused by more than just the viscosity change. In contrast, note that for the non-phosphonium, nitrogen-based cation, MPPipTf2N solutions, the overall change in the activation energy for conductivity and viscosity are similar (34.2 – 16.7) 17.5 for conductivity and (37.6 – 19.8) 17.8 for viscosity. Also, from the literature values of N-butyl-pyridinium dicyanamide / propylene carbonate solutions,[11] the overall change in the activation energy for the conductivity and viscosity are similar 12.6 for conductivity and 10.5 kJ for viscosity. This suggest that in these nitrogen-based cation ionic liquids changes in the conductivity are more related to the viscosity changes.

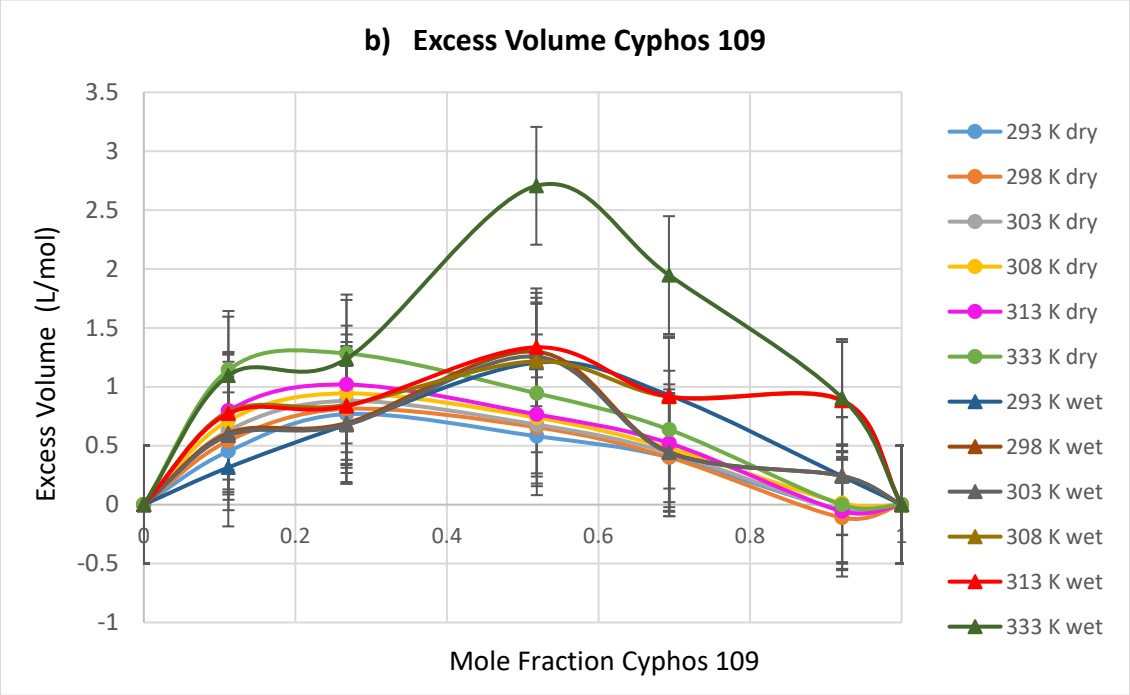
Derived Thermodynamic Parameters

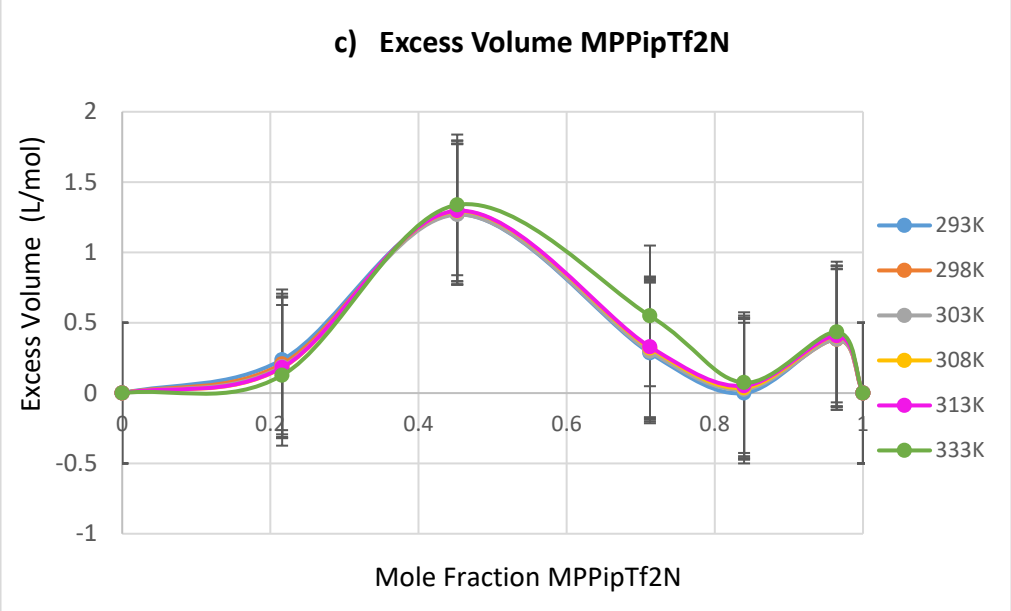
The molar excess volume V^E is related to the deviation of the experimentally derived volume, from the ideal volume of the solution. The excess volume can be calculated by Eqn. 2.

$$V^E = (x_{IL} M_{IL} + x_{PC} M_{PC}) / d_{soln} - [x_{IL} M_{IL}/d_{IL} + x_{PC} M_{PC}/d_{PC}] \quad (2)$$

where x_{IL} is mole fraction of ionic liquid in solution, M_{IL} is the molar mass of the ionic liquid, d_{IL} is the density of the ionic liquid and d_{soln} is the density of the solution. This assumes that the ideal volume is just a sum of the mole fraction times the molar volume for each of the components in the solution rather than the partial molar volume. A plot of the excess volume as a function of the mole fraction of ionic liquid in solution is shown for both Cyphos 105 and Cyphos 109 solutions in PC is given in Figures 5a-c. The error in the partial molar volume values were estimated through propagation of error. The error bars are essentially a constant error due to the uncertainty in the mole fraction times the molar mass.







Figures 5a-c. Plots of the excess molar volume as a function of mole fraction for a) Cyphos 105, b) Cyphos 109 and c) MPPipTf2N in PC at several temperatures.

For the wet Cyphos 105 solutions, the excess volume is negative at low mole fractions of Cyphos and oscillates between low positive and slightly negative values for higher mole fractions of Cyphos 105, whereas the excess volume is positive at almost all mole fraction of dried Cyphos 105 in solution. In contrast, the excess volume for **both** the wet and dry solutions containing

Cyphos 109 in PC are both almost exclusively positive except at the 99/1 concentration. For the MPPipTf2N solutions, the excess volume is strongly positive at low mole fractions becoming more positive at higher mole fractions, and finally decreasing and becoming almost zero at the 95/15 concentration. Thus, the solutions containing the bistriflimide anion, Cyphos 109 and MPPipTf2N have largely positive excess volume values except at the higher mole fraction solutions.

A positive excess molar volume indicates the molar volume of the mixture is larger than the ideal case. This would be expected when the solvent-solute attractive interaction is less than the solvent-solvent and the solute-solute interactions. The relative strengths of these types of interactions may vary as a function of the concentration due to the fact that the nearest neighbor and next-nearest-neighbor interactions will vary. The water content of the soln. may also affect the intermolecular interactions, perhaps most effectively if one of the ions in the IL is small and if the water concentration is higher. At low concentrations of the ionic liquid, ion pairing will likely be disrupted even for small anions such as dicyanamide interacting with the larger trihexyltetradecylphosphonium cation. At intermediate concentrations, the ion-pairing may be strong enough to overcome the disruptive presence of PC solvent and the volume shrinks and eventually the volume is less than the ideal volume due largely to the ion-pairing. This is the trend that is observed in the case of Cyphos 105 in PC. However, with Cyphos 109 and MPPipTf2N, the anion is the bistriflimide anion, which is bulkier than the dicyanamide ion in Cyphos 105. Thus, in the Cyphos 109 case, the larger anion and more polar solvent would likely prevent much of the ion-pairing from occurring, especially at lower temperatures, and so the excess molar volume would likely stay positive, even at high concentrations of the Cyphos 109 ionic liquid. This appears to be that case also for the MPPipTf2N ionic liquid. The bistriflimide anion in the piperidinium ionic liquid also appears to have a large effect on the excess volume being positive at most concentrations in PC. The large uncertainty in these values suggest caution when drawing any conclusions regarding differences in the values due to concentration changes, but confidence in the positive or negative nature of the excess volume for mole fractions near 0.5 is more justified. It should be noted, however, that a change of 5-10% in the solution mole fraction is enough to change the excess volume from negative to positive.

In addition to the excess molar volume, other thermodynamic parameters can be determined from the data. The molecular volume can be approximated by Equation 3,

$$V_{molecule} = M / (N_{av} \times d_{soln}) \quad (3)$$

where M is the molar mass of the ionic liquid, N_{av} is Avogadro's number and d is the density of the solution. The molecular volume can then be used, in Glasser's Theory,[20] to calculate the standard molar entropy of the ionic liquids by Equation 4.

$$S^0 = 1246.5\ V_{molecule} + 29.5 \quad (4)$$

and an approximation of the lattice energy is given by Equation 5

$$E_{lattice} = 1981.2\ (d_{IL}/M)^{1/3} + 103.8. \quad (5)$$

These values are provided in Table 8 for both Cyphos 105 and Cyphos 109 and also for MPPipTf2N ionic liquids. The calculated values for the molecular volume and the standard molar entropy for the Cyphos 105 are in reasonable agreement with the values of 1.1059 nm^3 and 1295.9 J/mol K reported by Pereiro et. al.[21]

Table 8. Molecular Volume, Molar Entropy and Molar Volume of Cyphos 105, Cyphos 109 and MPPipTf2N Ionic Liquids at 298 K. *Included in the table are these values for N-butyl pyridinium dicyanamide (BPD) ionic liquid from reference 11.

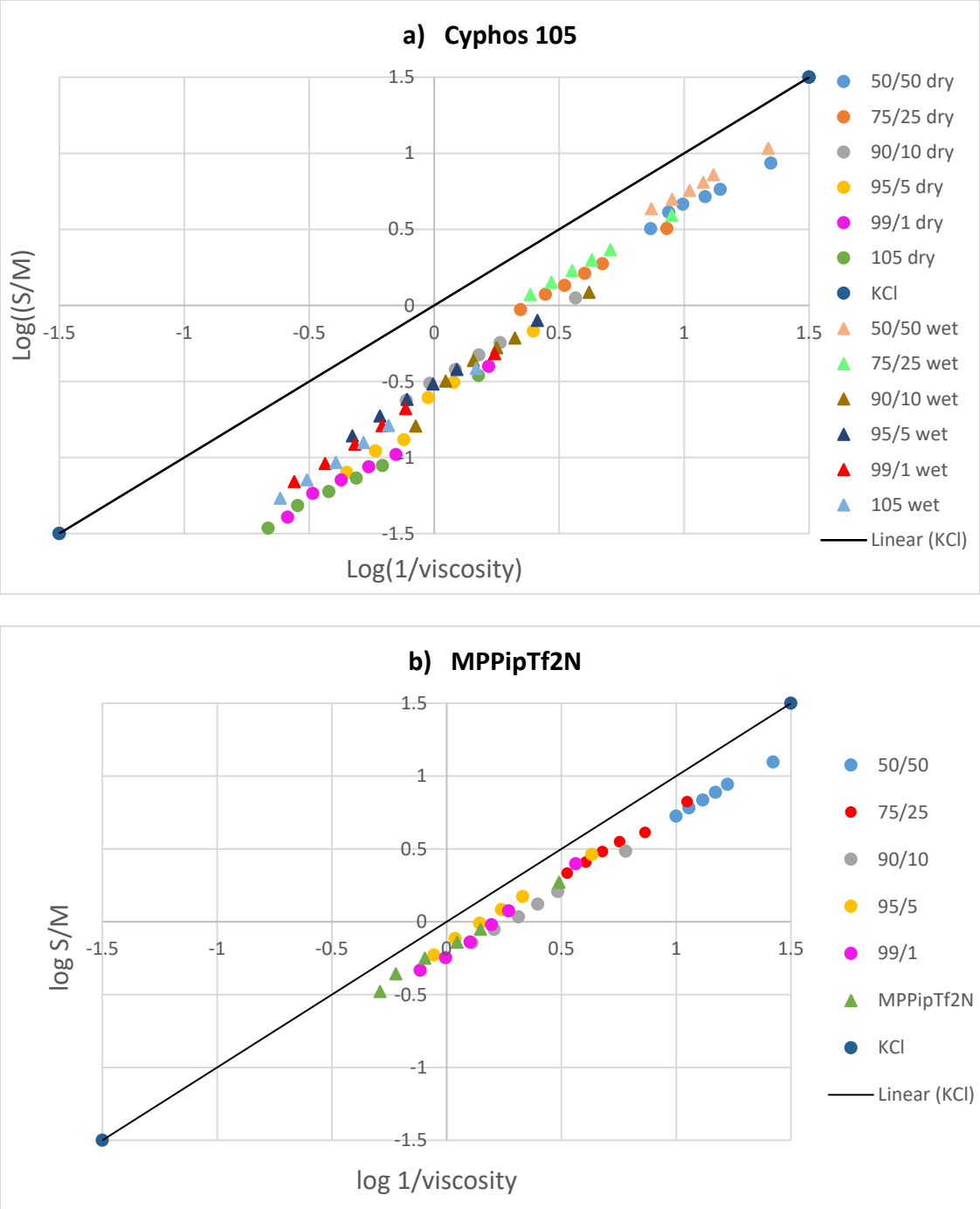
Ionic Liquid	Molecular Volume (nm^3)	Standard Molar Entropy (J/(mole K)	Molar Lattice Energy (kJ/mol)
Cyphos 105	1.022	1.30×10^3	337
Cyphos 109	1.195	1.52×10^3	325
MPPipTf2N	0.512	0.668×10^3	397
BPD*	0.314	0.421×10^3	449

Comparing these values with the N-butyl-pyridinium dicyanamide (BPD) ionic liquid in PC,[11] shows that the molecular volume of the Cyphos ionic liquids are significantly larger than the BPD and the lattice energy is lower. Also, the phosphonium ionic liquid with the larger anion, Cyphos 109, has a slightly larger molecular volume and standard molar entropy, but a lower lattice energy than Cyphos 105. The MPPipTf2N ionic liquid has a molecular volume that is about half that of Cyphos 105, but larger than the pyridinium ionic liquid. This may be due in part to the larger anion. The values of the molecular volume and molar entropies of the Cyphos liquids are consistent with the larger cation-anion pairs having a larger molecular volume and a larger entropy due to more degrees of geometrical freedom The lower lattice energies of the phosphonium ionic liquids are consistent with the interaction in these phosphonium ionic liquids being a largely constant, nearest-neighbor type interaction (ion-pairing), whereas the higher lattice energy in the piperidinium and pyridinium ionic liquid would promote longer range structure (mesostructured domains) which would change significantly as a function of the concentration of solvent present. The lattice energy of the pyridinium salt is still significantly lower than an average salt like sodium chloride (lattice enthalpy 787 kJ/mol) or CsI (lattice enthalpy 604 kJ/mol).

Ionicity and Electrochemical Attributes

The degree of ionicity of an ionic liquid is very important if the liquid is to be used as a medium for electrochemical processes such as reduction of metals. The ionicity will be a function of several physical properties of the solution dictated in part by the structure of the cation and anion of the ionic liquid. A common way to specify the degree of ionicity is to construct a log-log plot of the molar conductivity vs. 1/viscosity of the solution.[22] This Walden Plot can then be compared to a 0.01 M KCl solution which is the standard example for complete dissociation. Walden Plots for Cyphos 105 and MPPipTf2N ionic liquids as well as for their solutions in propylene carbonate at several temperatures are shown in Figure 6. The Walden Plots for all of the Ils studied (including Cyphos 109) are provided in Figures 5a-c in the Supplemental Information section. Note that the ionicity was generally higher in wet Cyphos 105 and 109 solns. except notably for neat Cyphos 109. The Walden plot for the MPPipTf2N ionic liquid and its solutions in PC was closer to the KCl line than for both of the Cyphos ionic liquids and solutions. This is expected since the MPPipTf2N ionic liquid and its solutions in PC have a lower viscosity and higher conductivity than the Cyphos ionic liquid solutions. However, the trend with increasing dilution in PC is different for the phosphonium IL than for the piperidinium IL. For the MPPipTf2N solutions, the deviation from the KCl line is slight, and the most dilute solution appears to deviate furthest from the KCl line. The Cyphos solutions have the opposite trend, and move closer to the KCl line with increasing dilution in PC. This is likely due to the larger decrease in viscosity and increased mobility of the ions in the Cyphos ionic liquid when mixed with PC. A different intermolecular arrangement could also contribute to this. If ion pairing is more prevalent in the Cyphos ionic liquids, then dilution would provide for better

solvation of the individual ions, allowing for the ions to move current more effectively with increasing dilution. A similar trend of increased ionicity in the Walden Plot (just two data points 1 M and .16 M solns.) was observed by Kobayashi et al for tributyllaurylphosphonium bis(trifluoromethanesulfonyl)imide in propylene carbonate.[23]



Figures 6a-b. Walden Plots showing the ionicity for a) Cyphos 105 and b) MPPipTf2N ionic liquids and solutions in PC at 203, 298, 303, 308, 313, and 333 K. The KCl line represents the standard for complete dissociation.

The electrochemical windows of several of the solutions were also measured, and they are given in Table 9. Here the electrochemical window is defined as the voltage region where the current remains less than 0.01mA/cm^2 at the working electrode.

Table 9. Values of the Electrochemical Windows for the pure substances and the solutions at 295 K. Solution labels are volume Cyphos IL to volume PC ratios.

Cyphos IL soln	Window wet (V)	Window dry (V)	Cyphos IL soln	Window wet (V)	Window Dry (V)	IL soln	Window Volts
105	3.5	3.7	109	4.5	4.3	MPPipTf2N	5.2 [24]
95/5	3.4	3.5	95/5	3.5	4.7	95/5	5.5
75/25	3.3	3.5	75/25	3.7	5.3	75/25	5.1
50/50	3.7	4.2	50/50	3.7	4.7	50/50	4.4

In this case the area of the glassy carbon working electrode is 0.071 cm^2. These are the voltages where the current remains between +0.71 micro-amps and -0.71 micro-amps. A typical cyclic voltammogram is given in Figure 7 with a magnified view of the region of the plot used to determine the electrochemical window at a temperature of 295 K.

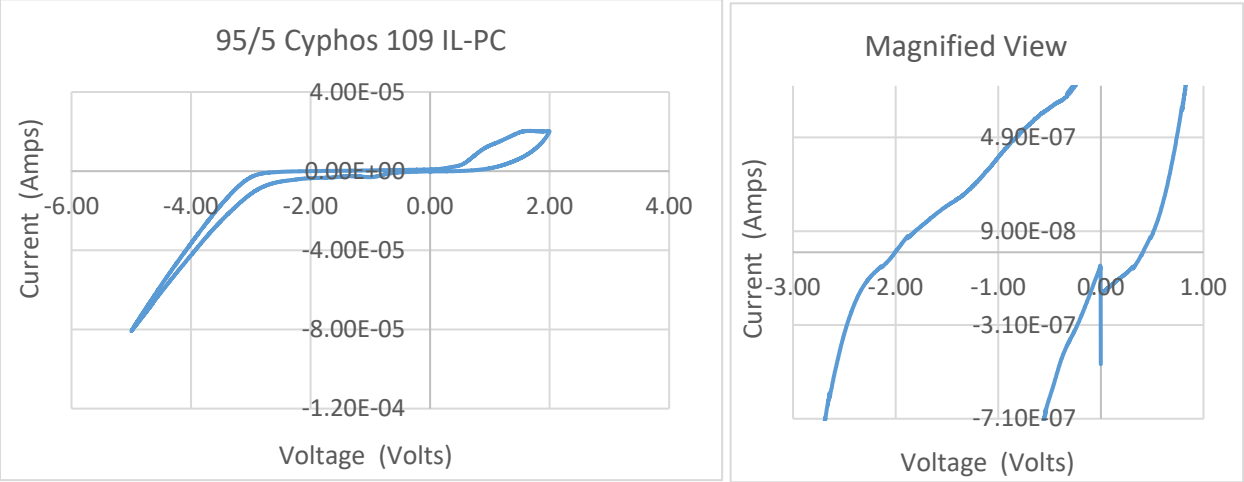


Figure 7. Typical cyclic voltammogram and magnified view of the region of the plot used to determine the electrochemical window.

The Cyphos 105 values were based on just the first CV trace. On the second and subsequent cycles, the CV trace overlapped itself. An overlapping trace often indicates some nucleation, and upon removing the working electrode from the solution, one could observe a deposit present on the electrode. The MPPipTf2N solutions have a larger electrochemical window than the Cyphos ionic liquid solutions and Cyphos 105 solns. are lower than Cyphos 109 solns. This is consistent with trends previously observed for other ionic liquids with the dicyanamide anion.[25] The window is also generally larger for the dried Cyphos solns. The small amount of water may result in very small but measurable oxidation and reduction currents at lower values of the oxidation and reduction potentials. If the process is reversible and the diffusion of the oxygen/hydrogen is not inhibited then the current due to oxidation or reduction of the water could be larger than the threshold value for the electrochemical window, and the electrochemical

window would be similar to that of water which is 1.23 V. Based on the Randles Sevcik Eqn,[26] the current could be on the order of 10^{-3} or 10^{-4} amps for an IL solution that has 1200 ppm H_2O at 298 K. However, if the produced oxygen and/or hydrogen are adsorbed on the electrode or on other species present, then diffusion is inhibited, and a "diffusion limited" eqn. must be used to calculate the current.[26] Based on the "diffusion limited" eqn. for adsorbed cases, the current could be much smaller, as low as 10^{-8} or 10^{-9} amps.[26] The measured electrochemical window of both the wet and dry IL solutions is much larger than what would be expected from water, so the water oxidation/reduction is probably diffusion inhibited, and it is likely that the reduction and oxidation processes of the ILs or solvent would be slightly affected by the presence of adsorbed oxygen or hydrogen.[27,28] This has been noted by other researchers investigating the effect of water on the electrochemical windows of ILs, and generally results in a narrower window.[28]

Overall the error associated with the measurements of the electrochemical windows due to environmental factors could be as large as 5-10% and so small changes in the values with a change in concentration may be within the expected error. All three ionic liquid solutions have sizeable windows. This lends well to the idea of using them for the conductive medium for recovery of metals by electrochemical methods.

Summary

The viscosity, conductivity, and density measurements for two phosphonium ionic liquids, Cyphos 105 and Cyphos 109, both with and without removal of water content, and also for "as-supplied" MPPipTf2N, were gathered for the neat ionic liquids and for 99/1, 95/5, 90/10, 75/25, and 50/50 v/v mixtures of these ionic liquids with PC. These measurements along with cyclic voltammetry measurements were used to calculate kinetic, thermodynamic, and electrochemical properties of these solutions.

It was found that the viscosities of the MPPipTf2N solutions were 30% lower than the Cyphos solutions and the conductivity values for the solutions were between 2, at higher temps., and 4, at lower temps., times higher for the MPPip solutions. For both types of solutions, the viscosity decreased and the conductivity increased as the concentration of ionic liquid in PC solution decreased. The large change in viscosity leads to higher conductivity, and an additional contribution to the enhanced conductivity for Cyphos solutions at low concentrations is the lower lattice energy than the piperidinium and pyridinium ionic liquids. This lower lattice energy likely leads to less mesostructured domains and a higher conductivity at increased dilution.

The temperature dependence of both the viscosity and the conductivity largely followed an Arrhenius relationship. For the phosphonium IL solutions, the change in the activation energy for conduction between the lowest IL concentration and pure IL is larger than the change in the activation energy associated with the viscosity between those same two concentration extremes. However, this is not the case for the piperidinium IL solutions. The larger activation barrier difference would be expected if the phosphonium IL had a larger contribution from ion pairing that had to be overcome for conduction to occur, whereas movement of the meso bilayer conductive sheets of the liquid past each other would be more related to the viscosity activation energy. Although the phosphonium cation-based ILs have been observed to have some mesoscopic structure due to interdigitation of alkyl tails of two neighboring cations,[26] the nitrogen-based MPPip IL, is expected to have more ionic mesostructured layering as with other nitrogen cation-based ILs,[26] and the activation barriers for both movement of the sheets of liquid past one another (viscosity) and the conduction of current (conductivity) would be very similar. Essentially movement of the conductive sheet would also constitute movement of charge. Thus, the activation barrier change difference are suggestive that although ion clusters and solvated ions

are present in both types of ionic liquids, ion pairing is occurring to a larger extent in the phosphonium IL and mesostructured layering occurs more in the piperidinium IL.

Other studies of solutions of nitrogen cation- based ionic liquid/propylene carbonate solutions have reported somewhat similar observations. In the studies by Lam et. al,[2] the activation energy of the ion motion for the ionic liquids was reduced as the PC concentration was increased. They concluded that the increase in the PC/IL solution conductivity therefore came from the lower activation energy. They did not compare the activation energy determined from the viscosity to that determined from the conductivity. They mentioned that in other systems with solvents like acetic acid, the increase in PC/IL conductivity comes from "the high number of charge carriers, 'freed' from ion clusters when acetic acid is added." Here the lower activation energy of the ion motion might be a result of weaker interactions between the solvated ions, and the increased conductivity, as a result of more PC added, is due to a reducing of that part of the activation energy related to intermolecular interactions. These interactions can be electrostatic as in ion pairing and in the case of Cyphos 105 and 109, the solvent could also break the intermolecular forces associated with interdigitation of the alkyl tails.[29]

There appeared to be a significant change in the excess volume between the wet and dry Cyphos 105 solns., changing from negative at higher dilutions in PC to almost exclusively positive at all dilutions in the dry solns. although the error in these measurements was rather large. This was not the case for the Cyphos 109 solns. This suggests that water can play a significant role in the intermolecular interactions, especially for Ils that contain more compact anions. It should be noted that the excess volume calculation is very sensitive to the mole fraction used and an error of 10% in the mole fraction could cause the excess volume to change from negative to positive.

The Walden plots proved to be most interesting and showed an enhancement in the ionic conduction at higher dilutions for both of the Cyphos solutions. The Cyphos solutions have the opposite trend from the MPPipTf2N solutions, moving closer to the KCl line with increasing dilution in PC. This increased mobility of the Cyphos ionic liquid suggests a different intermolecular arrangement than in the MPPipTf2N solutions. If, as was the conclusions from the activation energy differences, ion pairing is more prevalent in the Cyphos ionic liquids, then dilution provides for much better solvation and separation of each ion of the ion pairs in the phosphonium ILs which is a significant boost to the ionicity and conductivity of this solution as the activation barrier to movement of charge is significantly lower in the solution. In contrast, the conclusion that the MPPip IL formed layered charged mesostructures, the conduction and ionicity might decrease if the charged layers were broken apart.

The electrochemical windows were measured and showed that the MPPipTf2N solutions had the highest electrochemical window with a small decrease in the window from 5.2 V to 4.4 V at the highest dilution. This high electrochemical stability over this concentration range, along with its lower viscosity and increased conductivity suggest ionic liquid solutions of MPPipTf2N in PC would be good for the electrodeposition of metals. The electrochemical window was near 4 V for both the Cyphos 105 and near 4 or 5 V for Cyphos 109 and did have a large change in going from the 95/5 to the 50/50 v/v mixtures. The dried Cyphos solns. generally had a larger electrochemical window. The measured electrochemical window of both the wet and dry IL solutions is much larger than what would be expected from water alone, leading to the conclusion that the water oxidation/reduction must be diffusion inhibited. The differences in the reduction and oxidation processes of the IL solutions with water suggest that the oxidation and reduction processes of the IL solutions are likely slightly affected by the presence of adsorbed

oxygen or hydrogen. The increasing conductivity at low concentration and the large electrochemical window features of the Cyphos 105 and Cyphos 109 phosphonium-based ionic liquid solutions should also make them reasonable candidates for further investigation as an ionic liquid solution suitable for electrodeposition of metals even with their reduced conductivity relative to the MPPipTf2N solutions. Although there were not significant changes between the densities of the wet and dried Cyphos solutions, other properties and thermodynamic and kinetic parameters are affected by the water content in the phosphonium Ils.

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References
1. L.G. Sanchez, J.R. Espel, F. Onink, G.W. Meindersma, Density, viscosity, and surface tension of synthesis grade imidazolium, pyridinium, and pyrrolidinium based room temperature ionic liquids, J. Chem. Eng. Data 54 (2009) 2803–2812.
2. P. Lam, A. Tran, D. Walczyk, A. Miller, L. Yu, Conductivity, viscosity, and thermodynamic properties of propylene carbonate solutions in ionic liquids, Journal of Molecular Liquids, 246 (2017) 215–220.
3. J. Barthel, R. Neueder, H. Roch, Density, Relative Permittivity, and Viscosity of Propylene Carbonate + Dimethoxyethane Mixtures from 25 °C to 125 °C, J. Chem. Eng. Data 45 (2000) 1007-1011.
4. K. Kuribara, M. Matsumiya, K. Tsunashima, Solvation structure and thermodynamics for Pr(III), Nd(III) and Dy(III) complexes in ionic liquids evaluated by Raman spectroscopy and DFT calculation, Journal of Molecular Structure, 1125 (2016) 186-192.
5. L.Y. Sun, O. Morales-Collazo, H. Xia, J.F. Brennecke, Effect of structure on transport properties (viscosity, ionic conductivity and self-diffusion coefficient) of aprotic heterocyclic anion (AHA) room temperature ionic liquids. 2. Variation of alkyl chain length in the phosphonium cation, J. Phys. Chem. B 120 (2016) 5767–5776.
6. R. Kasama, M. Matsumiya, N. Tsuda, K. Tsunashima, Electrochemical analysis of diffusion behavior and nucleation mechanism for Dy(II) and Dy(III) in phosphonium-based ionic liquids, Electrochim. Acta 113 (2013) 269-279.
7. H. Kondo, M. Matsumiya, K. Tsunashima, S. Kodama, Investigation of oxidation state of the electrodeposited neodymium metal related with the water content of phosphonium ionic liquids, ECS Transactions, 50 (11) (2012) 529-538.
8. J. Tang, D. Lv, C. Xu, Y. Hua, Q. Zhang, P Niu, X. Zhu, The effect of water on the tin electrodeposition from [Bmim] HSO4 Ionic Liquid, International Journal of Electrochemistry, (2018) 1-7. https://doi.org/10.1155/2018/1210394
9. Y. Cui, Y. Hua, Y. Lin, Applications of ionic liquids in electrodeposition of rare earths, Journal of Chongqing University: Eng Ed [ISSN 1671-8224] (2010) 9(4): 167-176.
10. T. Yamamura, M. Mehmood, H. Maekawa, Y. Sato, Electrochemical processing of rare earths and rare metals by using molten salts, Chemistry for Sustainable Development 12 (2004) 105-111.
11. Q. Zhang, Q. Li, D. Liub, X. Zhang, X. Lang, Density, dynamic viscosity, electrical conductivity, electrochemical potential window, and excess properties of ionic liquid N-butyl-

pyridinium dicyanamide and binary system with propylene carbonate, Journal of Molecular Liquids 249 (2018) 1097–1106.
12. N. Calvar, E.J. González, Á. Domínguez, E.A.Macedo, Acoustic, volumetric and osmotic properties of binary mixtures containing the ionic liquid 1-butyl-3-methylimidazolium dicyanamide mixed with primary and secondary alcohols, J. Chem. Thermodyn. 50 (2012) 19–29.
13. N. Zec, M. Bešter-Rogač, M. Vraneš, S. Gadžurić, Volumetric and viscosimetric properties of [bmim][DCA] + γ-butyrolactone binary mixtures, J. Chem. Thermodyn. 97 (2016) 307–314.
14. M. Vraneš, N. Zec, A. Tot, S. Papović, S. Dožić, S. Gadžurić, Density, electrical conductivity, dynamic viscosity and excess properties of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + propylene carbonate binary mixtures, J. Chem. Thermodyn. 68 (2014) 98–108.
15. A. Podgoršek, J. Jacquemin, A.A.H. Pádua, M.F. Costa Gomes, Mixing enthalpy for binary mixtures containing ionic liquids, Chem. Rev. 116 (2016) 6075–6106.
16. M.S. Reddya, K.T.S. Raju, A.S. Rao, N. Sharmila, B.H. Babu, Study of thermophysical properties of the binary mixtures of ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate and 2-propoxyethanol from T = (298.15 to 328.15) K at atmospheric pressure, J. Chem. Thermodyn. 101 (2016) 139–149.
17. R. Hayes, G. Warr, R. Atkin, Structure and Nanostructure in Ionic Liquids, Chem. Rev., 115 (2015) 6357-6426.
18. K. Fraser, E. Izgorodina, M. Forsyth, J. Scott, D. MacFarlane, Liquids intermediate between “molecular” and “ionic" liquids: Liquid Ion Pairs?, Chem. Comm. (2007) 3817-3819
19. K. Shimizu, M. F. Costa Gomes, A. A. Padua, L. P. N Rebelo, J. N. J. Canongia Lopes, Three Commentaries on the nano-segregated structure of ionic liquids, J. Mol. Struct. (THEOCHEM) 946 (2010) 70− 76.
20. L. Glasser, Lattice and phase transition thermodynamics of ionic liquids, Thermochim. Acta 421 (2004) 87–93.
21. A. Pereiro, H.Veiga, J. Esperança, A. Rodríguez, Effect of temperature on the physical properties of two ionic liquids, J. Chem. Thermodynamics 41 (2009) 1419–1423
22. D. MacFarlane, M. Forsyth, E. Izgarodina, A. Abbott, G. Annat, and K. Fraser, On the concept of ionicity in ionic liquids, Phys. Chem. Chem. Phys., 11 (2009) 4962-4967.
23. Y. Kobayashi, S. Tokishita, H. Yamamoto, Determination of Hansen Solubility Parameters of Ionic Liquids by Using Walden Plots, Ind. Eng. Chem. Res. 59 (2020) 14217−14223
24. T. Yim, H. Y. Lee, H. Kim, J. Mun, S. Kim, S. M. Oh, and Y. G. Kim, Synthesis and Properties of Pyrrolidinium and Piperidinium Bis(trifluoromethanesulfonyl)imide Ionic Liquids with Allyl Substituents, Bull. Korean Chem. Soc. 28 (2007) 1567-72.
25. M. Hayyan, F. S. Mjalli, M. A Hashim, I. M. AlNashef, T. X. Mei, Investigating the electrochemical windows of ionic liquids, Journal of Industrial and Engineering Chemistry 19 (2013) 106–112.
26. N, Elgrishi,́ K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, J. L. Dempsey A Practical Beginner’s Guide to Cyclic Voltammetry, J. Chem. Educ. 95 (2018) 197−206
27. S. Randstrom, M. Montaninoa, G. B. Appetecchi, C. Lagergrenb,, A. Morenoa, S. Passerini, Effect of water and oxygen traces on the cathodic stability of N-alkyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, Electrochimica Acta 53 (2008) 6397–6401

28. A. M. O'Mahony, D. S. Silvester, L. Aldous, C. Hardacre, R. G. Compton, Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids, J. Chem. Eng. Data, 53 (2008) 2884–2891
29. T. Cosby, Z. Vicars , M. Heres, K. Tsunashima, and J. Sangoro, Dynamic and structural evidence of mesoscopic aggregation in phosphonium ionic liquids, J. Chem. Phys. 148, (2018) 193815.

Supplemental Information

Table 1a. Densities (in g/mL) of the Cyphos 105/PC solutions as a function of temperature concentration, and water content.

Temp K	50/50 soln.	75/25 soln.	90/10 soln	95/5 soln.	99/1 soln.	Cyphos 105
1200 ppm H_2O						
293	1.048	0.975	0.932	0.914	0.902	0.899
313	1.028	0.957	0.916	0.898	0.886	0.883
333	1.008	0.940	0.899	0.882	0.871	0.868
17 ppm H_2O						
293	1.045	0.973	0.929	0.914	0.902	0.899
313	1.026	0.955	0.912	0.898	0.887	0.884
333	1.006	0.937	0.896	0.882	0.871	0.868

Table 1b. Densities (in g/mL) of the Cyphos 109/PC solutions as a function of temperature, concentration, and water content

Temp K	50/50 soln	75/25 soln	90/10 soln	95/5 soln	99/1 soln	Pure Cyphos 109
600 ppm H_2O						
293	1.131	1.097	1.077	1.071	1.067	1.066
313	1.108	1.077	1.057	1.052	1.047	1.047
333	1.086	1.056	1.035	1.031	1.028	1.028
32 ppm H_2O						
293	1.134	1.098	1.079	1.073	1.068	1.067
313	1.111	1.078	1.060	1.054	1.049	1.048
333	1.089	1.058	1.040	1.035	1.030	1.029

Table 1c. Densities (in g/mL) of the MPPipTf2N/PC solutions as a function of the temperature and concentration.

Temp K	50/50 soln	75/25 soln	90/10 soln	95/5 soln	99/1 soln	Pure MPPipTf2N
293	1.3077	1.3537	1.3931	1.405	1.4119	1.4159

313	1.284	1.3302	1.3697	1.382	1.389	1.393
333	1.2603	1.3068	1.3457	1.3592	1.3664	1.3705

Table 2a. Concentration of the Cyphos 105 Solutions in terms of the volume ratio, molarity, and mole fraction. Values given are at 293 K.

Volume Ratio V_{IL}/V_{PC} Soln. Conc.	Wet Solution Molarity mol(IL)/L(soln)	Dry Solution Molarity mol(IL)/L(soln)	Mole Fraction Wet Ionic Liquid	Mole Fraction Dry Ionic Liquid
50/50	0.747	0.811	0.121	0.125
75/25	1.17	1.22	0.293	0.295
90/10	1.44	1.47	0.555	0.552
95/5	1.53	1.55	0.724	0.719
99/1	1.61	1.62	0.932	0.937
Pure 105	1.63	1.63	1.00	1.00

Table 2b. Concentration of the Cyphos 109 Solutions in terms of the volume ratio, molarity, and mole fraction. Values given are at 293 K.

Volume Ratio V_{IL}/V_{PC} Soln. Conc.	Wet Solution Molarity mol(IL)/L(soln)	Dry Solution Molarity mol(IL)/L(soln)	Mole Fraction Wet Ionic Liquid	Mole Fraction Dry Ionic Liquid
50/50	0.694	0.697	0.106	0.102
75/25	1.04	1.04	0.262	0.261
90/10	1.25	1.26	0.515	0.515
95/5	1.32	1.33	0.692	0.691
99/1	1.38	1.38	0.921	0.940
Pure 109	1.39	1.40	1.00	1.00

Table 2c. Concentration of the MPPipTf2N Solutions in terms of the volume ratio, molarity, and mole fraction. Values given are at 293 K.

Volume Ratio V_{IL}/V_{PC} Soln. Conc.	Solution Molarity mol(IL)/L(soln)	Mole Fraction Dry Ionic Liquid
50/50	1.62	0.215
75/25	2.42	0.452
90/10	2.92	0.712
95/5	3.08	0.840
99/1	3.21	0.965
Pure MPPipTf2N	3.25	1.00

Table 3a. Solution viscosity (in mPa s) as a function of temperature and IL/PC v/v concentration for Cyphos 105 in PC.

Temp K	50/50 wet	dry	75/25 wet	dry	90/10 wet	dry	95/5 wet	dry	99/1 wet	dry	Pure wet	dry
293	13.5	13.6	41.3	45.3	119	129	212	223	363	386	413	461

298	11.2	11.5	34.0	35.9	89.9	104	165	172	273	306	323	352
303	9.51	10.1	28.1	30.1	69.7	82.1	128	132	208	235	247	264
308	8.39	8.24	23.4	25.0	56.2	66.2	101	106	162	183	192	205
313	7.63	7.16	19.7	21.2	47.6	54.4	81.1	83.5	130	142	152	161
333	4.61	4.50	11.2	11.7	24.0	27.2	38.6	40.1	57.3	60.5	67.9	66.5

Table 3b. Solution viscosity (in mPa s) as a function of temperature and IL/PC v/v concentration for Cyphos 109 in PC.

Temp K	50/50 wet	dry	75/25 wet	dry	90/10 wet	dry	95/5 wet	dry	99/1 wet	dry	Pure wet	dry
293	13.4	11.5	39.5	39.3	130	118	209	207	352	366	378	413
298	11.0	8.80	32.4	32.1	96.7	91.9	160	158	265	273	300	302
303	9.23	7.91	26.8	27.6	72.9	75.0	124	121	202	215	230	235
308	7.89	6.94	22.4	22.8	56.7	61.2	97.5	96.6	158	166	186	188
313	6.89	6.14	19.0	19.0	46.1	48.8	79.3	77.3	128	130	142	144
333	4.24	3.86	10.6	10.2	23.5	24.7	37.7	36.9	56.1	57.1	63.7	60.9

Table 3c. Solution viscosity (in mPa s) as a function of temperature and IL/PC v/v concentration for MPPipTf2N in PC.

Temp. K	50/50	75/25	90/10	95/5	99/1	100
293	10.0	29.8	77.5	114	130	195
298	8.80	24.7	62.1	91.8	101	167
303	7.66	21.0	48.6	71.7	79.0	124
308	6.74	17.6	40.1	57.7	63.8	90.0
313	5.97	13.7	32.8	46.7	53.6	71.2
333	3.78	8.96	16.6	23.3	27.4	32.3

Table 4a. Energies of Activation and Pre-exponential Factors Derived from *viscosity* data fitted to the Arrhenius and Litovitz eqns. for the Cyphos 105 wet and dry solutions in PC.

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
50/50	21.3	22.7	6.93e5	7.37e5	2.07e-3	1.22e-3	4.89e-1	4.06e-1
75/25	26.5	27.1	8.65e5	8.81e5	7.68e-4	6.52e-4	6.80e-1	6.72e-1
90/10	32.0	31.7	1.04e6	1.03e6	2.24e-4	2.81e-4	8.03e-1	9.56e-1
95/5	34.6	34.9	1.12e6	1.13e6	1.40e-4	1.33e-4	9.95e-1	1.00e0
99/1	37.3	38.0	1.21e6	1.23e6	7.93e-5	6.71e-5	1.12e0	1.13e0
Cyphos105	36.8	40.4	1.20e6	1.28e6	1.12e-4	2.88e-5	1.40e0	1.06e0

Table 4b. Energies of Activation and Pre-exponential Factors Derived from *viscosity* data fitted to the Arrhenius and Litovitz eqns. for the Cyphos 109 wet and dry solutions in PC.

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
50/50	23.1	21.2	7.51e5	6.90e5	9.91e-4	1.78e-3	3.64e-1	4.07e-1
75/25	26.5	27.4	8.65e5	8.90e5	7.23e-4	5.05e-4	6.47e-1	5.76e-1
90/10	34.5	31.7	1.12e6	1.03e6	8.48e-5	2.56e-4	5.81e-1	8.70e-1
95/5	34.7	34.9	1.12e6	1.13e6	1.35e-4	1.22e-4	9.62e-1	9.19e-1
99/1	37.0	37.6	1.21e6	1.22e6	8.54e-5	7.12e-5	1.13e0	1.09e0
Cyphos109	36.4	38.5	1.18e6	1.25e6	1.23e-4	5.55e-5	1.39e0	1.07e0

Table 4c. Energies of Activation and Pre-exponential Factors Derived from *viscosity* data fitted to the Arrhenius and Litovitz eqns. for the MPPipTf2N solutions in PC.

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)	Litovitz Energy	Arrhenius Preexponential Factor	Litovitz Preexponential Factor
50/50	19.8	6.43e5	2.94e-3	4.74e-1
75/25	24.8	8.08e5	1.09e-3	6.22e-1
90/10	31.3	8.31e5	2.03e-4	6.13e-1
95/5	32.3	1.05e6	1.95e-4	7.70e-1
99/1	31.4	1.02e6	3.16e-4	9.98e-1
MPPipTf2N	37.6	1.22e6	3.95e-5	6.08e-1

Table 4d. Energies of Activation and Pre-exponential Factors Derived from literature *viscosity* and *conductivity* data fitted to the Arrhenius eqns. for N-butyl-pyridinium dicyanamide solutions in PC[11] Q. Zhang et al. / Journal of Molecular Liquids 249 (2018) 1097–1106

Soln. mole fraction	Arrhenius Energy (viscosity) (kJ/mol)	Litovitz Energy	Arrhenius Energy (conductivity) (kJ/mol)	Litovitz Preexponential Factor
0.10	15.0	6.43e5	12.6	4.74e-1
0.30	18.3	8.08e5	15.6	6.22e-1
0.50	21.1	8.31e5	19.0	6.13e-1
0.70	23.5	1.05e6	21.4	7.70e-1
0.90	25.8	1.02e6	23.1	9.98e-1
n-butyl-pyridinium dicyanamide	25.5	1.22e6	25.4	6.08e-1

Table 5a. Solution conductivity (in mS/m) as a function of temperature and concentration for Cyphos 105 wet and dry solns. in PC.

Temp K	50/50 wet	dried	75/25 wet	dried	90/10 wet	dried	95/5 wet	dried	99/1 wet	dried	Pure wet	dried
293	351	259	144	114	23.7	34.8	21.5	12.3	11.2	6.5	8.8	5.6
298	403	331	173	144	46.6	44.8	28.9	17.1	14.7	9.3	11.6	7.8
303	459	371	205	163	63.3	55	37.0	20.1	19.6	11.4	15.0	9.7
308	516	414	240	195	76.4	68.2	46.5	37.8	25.8	13.9	20.2	11.8
313	575	460	279	225	88.3	81.8	57.6	47.5	33.3	16.6	26.0	14.2
333	843	672	460	376	173	158	119	101	75.1	62.0	60.7	54.4

Table 5b. Solution conductivity (in mS/m) as a function of temperature and concentration for Cyphos 109 wet and dry solns. in PC.

Temp K	50/50 wet	dried	75/25 wet	dried	90/10 wet	dried	95/5 wet	dried	99/1 wet	dried	Pure wet	dried
293	222	200	92.6	76.4	16.3	21.7	15.3	9.6	8.4	4.7	6.94	5.0
298	255	230	113	102	29.8	34.2	21.0	14.2	11.3	7.4	9.03	7.3
303	294	261	136	121	42.4	41.5	28.5	17.3	14.9	9.2	11.8	9.2
308	335	293	161	142	54.6	50.8	36.0	20.9	19.9	11.5	17.6	10.9
313	379	326	189	164	66.9	64.0	43.1	36.6	26.6	14.2	19.1	13.5
333	571	476	324	273	124	127	105	76.6	57.9	43.8	48.7	42.9

Table 5c. Solution conductivity (in mS/m) as a function of temperature and concentration for MPPipTf2N solns. in PC.

Temp. K	50/50 soln	75/25 soln	90/10	95/5 soln	99/1 soln	Pure MPPipTf2N
293	860	521	209	181	149	108
298	975	618	257	236	181	142
303	1009	727	312	299	231	181
308	1235	845	380	368	302	232
313	1394	974	462	452	374	284
333	1951	1558	860	863	775	587

Table 6a. Energies of Activation and Pre-exponential Factors Derived from *conductivity* data fitted to the Arrhenius and Litovitz equations for Cyphos 105 wet and dry solns. in PC

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy (kJ/mol)		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
50/50	17.7	18.4	5.74e5	5.99e5	5.07e5	5.32e5	5.49e3	4.82e3
75/25	23.5	23.8	7.63e5	7.72e5	2.26e6	2.04e6	5.54e3	4.63e3
90/10	36.7	30.5	1.21e6	9.89e5	1.13e8	9.82e6	9.70e3	3.98e3
95/5	34.4	44.0	1.11e6	1.43e6	3.02e7	8.84e8	4.54e3	1.16e4
99/1	38.8	44.3	1.26e6	1.43e6	9.52e7	4.79e8	4.58e3	5.54e3
Cyphos105	41.5	45.0	1.28e6	1.45e6	2.14e8	5.39e8	3.87e3	5.17e3

Table 6b. Energies of Activation and Pre-exponential Factors Derived from *conductivity* data fitted to the Arrhenius and Litovitz equations for Cyphos 109 wet and dry solns. in PC

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)		Litovitz Energy (kJ/mol)		Arrhenius Preexponential Factor		Litovitz Preexponential Factor	
	wet	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
50/50	19.2	17.5	6.24e5	5.68e5	5.91e5	2.66e5	4.36e3	3.01e3
75/25	25.3	24.9	8.22e5	8.11e5	3.08e6	2.30e6	4.72e3	3.90e3
90/10	38.7	34.2	1.27e6	1.11e6	1.75e8	3.13e7	8.96e3	4.96e3
95/5	40.7	42.3	1.25e6	1.37e6	1.16e8	3.45e8	6.06e3	6.84e3
99/1	39.4	43.5	1.28e6	1.41e6	9.22e7	2.83e8	3.83e3	4.02e3
Cyphos109	39.4	42.2	1.28e6	1.36e6	7.40e7	1.68e8	3.07e3	3.29e3

Table 6c. Energies of Activation and Pre-exponential Factors Derived from *conductivity* data fitted to the Arrhenius and Litovitz equations for MPPipTf2N solns. in PC

Soln. Conc. V_{IL}/V_{PC}	Arrhenius Energy (kJ/mol)	Litovitz Energy (kJ/mol)	Arrhenius Preexponential Factor	Litovitz Preexponential Factor
50/50	16.7	5.43e5	8.22e5	1.14e4
75/25	22.2	7.21e5	4.78e6	1.63e4
90/10	28.8	9.31e5	2.86e7	1.79e4
95/5	31.4	1.02e6	7.58e7	2.43e4
99/1	34.0	1.11e6	1.72e8	2.69e4
MPPipTf2N	34.2	1.11e6	1.40e8	2.20e4

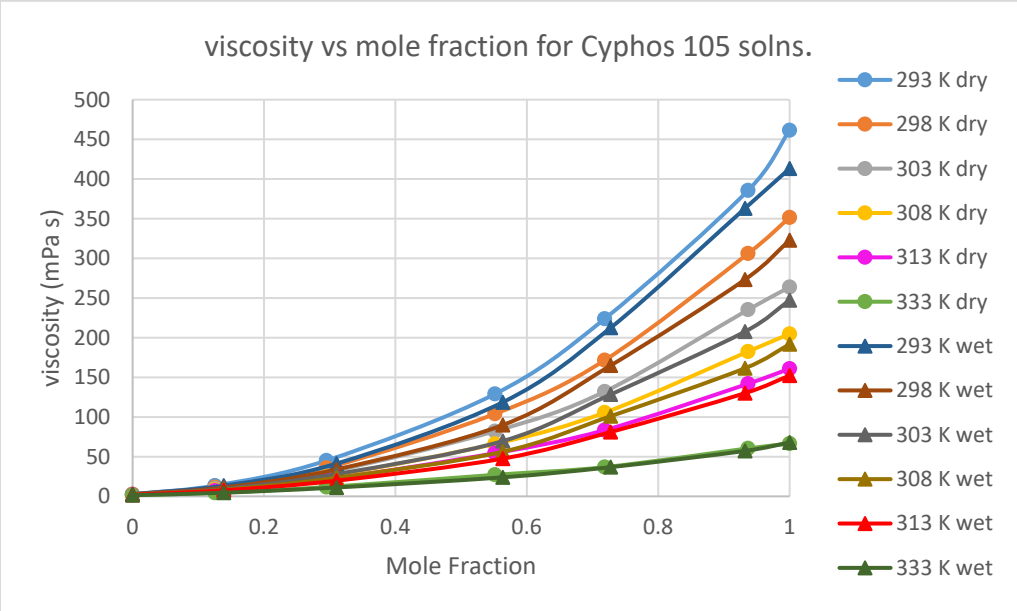

Figure 1a. Plot of the viscosity as a function of mole fraction IL for both wet and dried Cyphos 105 solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

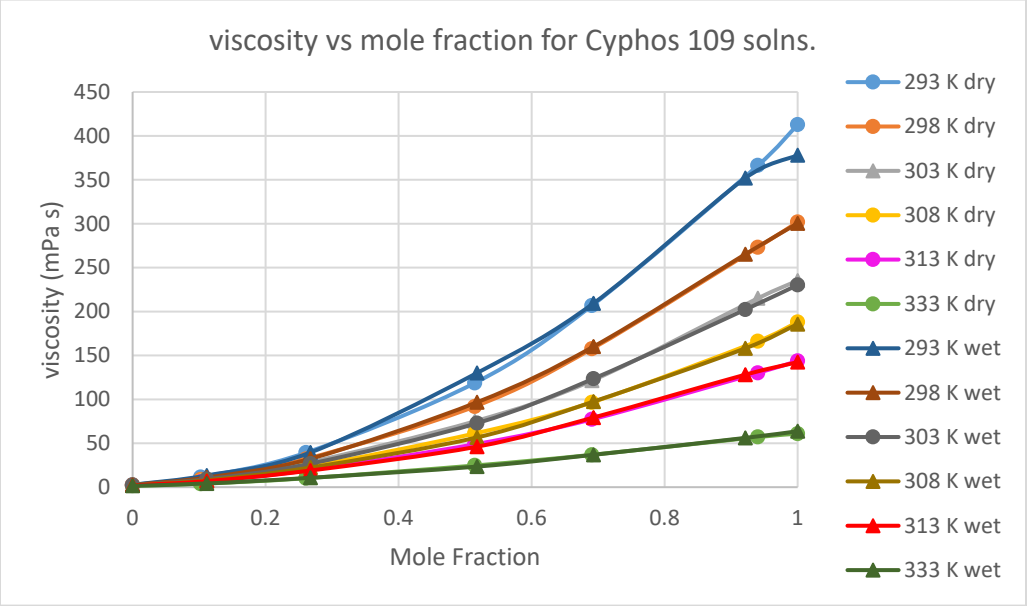

Figure 1b. Plot of the viscosity as a function of mole fraction IL for both wet and dried Cyphos 109 solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

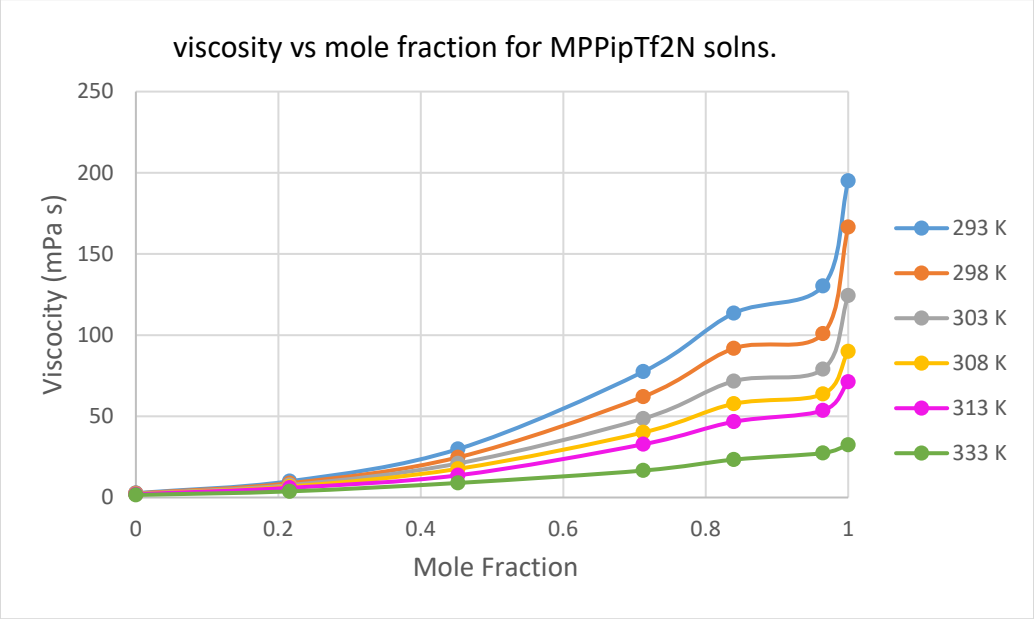

Figure 1c. Plot of the viscosity as a function of mole fraction IL for the MPPipTf2N solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

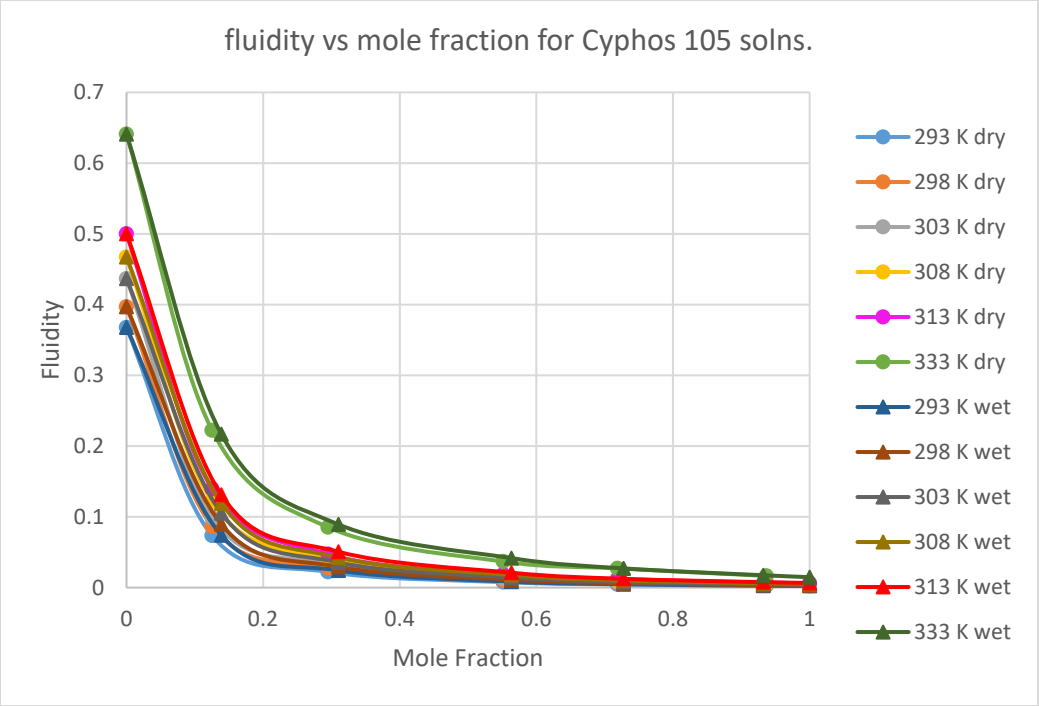

Figure 2a. Plot of the fluidity as a function of mole fraction for wet and dried Cyphos 105 solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K. The nonlinearity is suggestive of a non-ideal solution

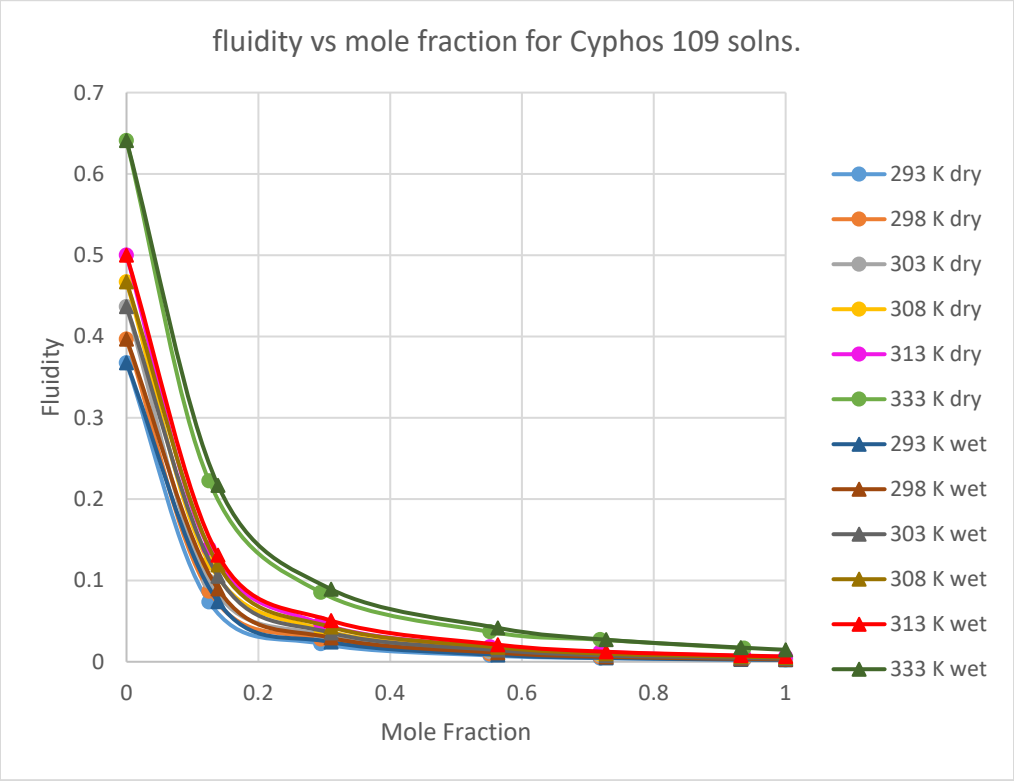

Figure 2b. Plot of the fluidity as a function of mole fraction for wet and dried Cyphos 109 solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K. The nonlinearity is suggestive of a non-ideal solution

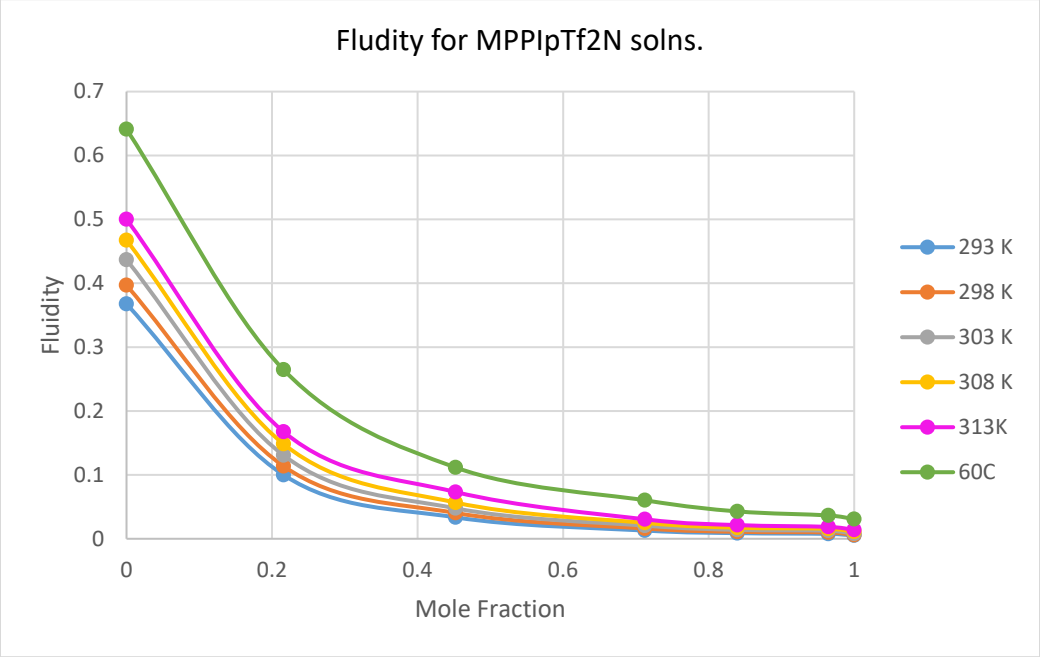

Figure 2c. Plot of the Fluidity as a function of mole fraction IL for the MPPipTf2N solutions in PC at temperatures of 293, 298, 303, 308, 313, and 333 K.

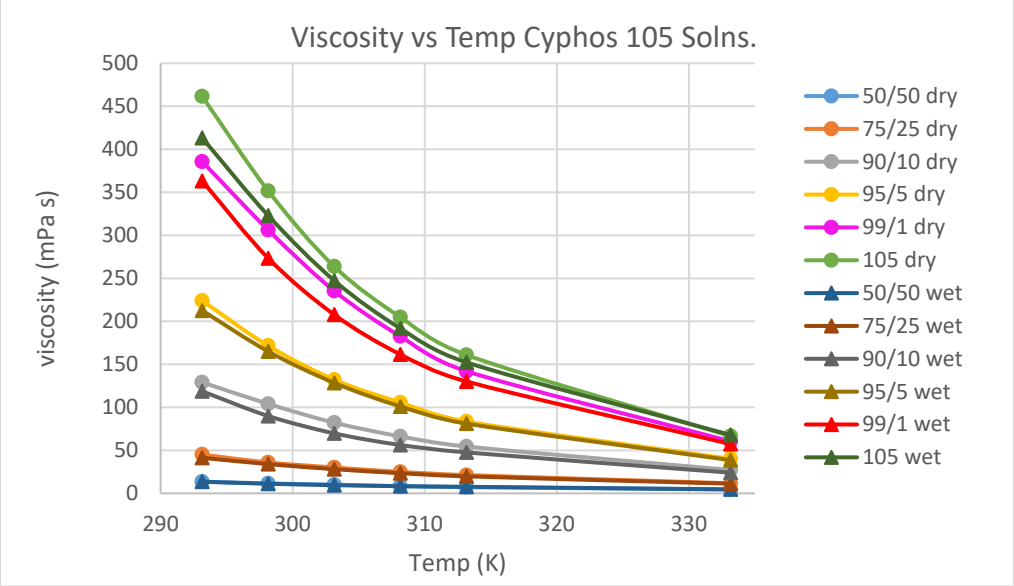

Figure 3a. Plot of the Viscosity vs Temp. for Cyphos 105 solutions

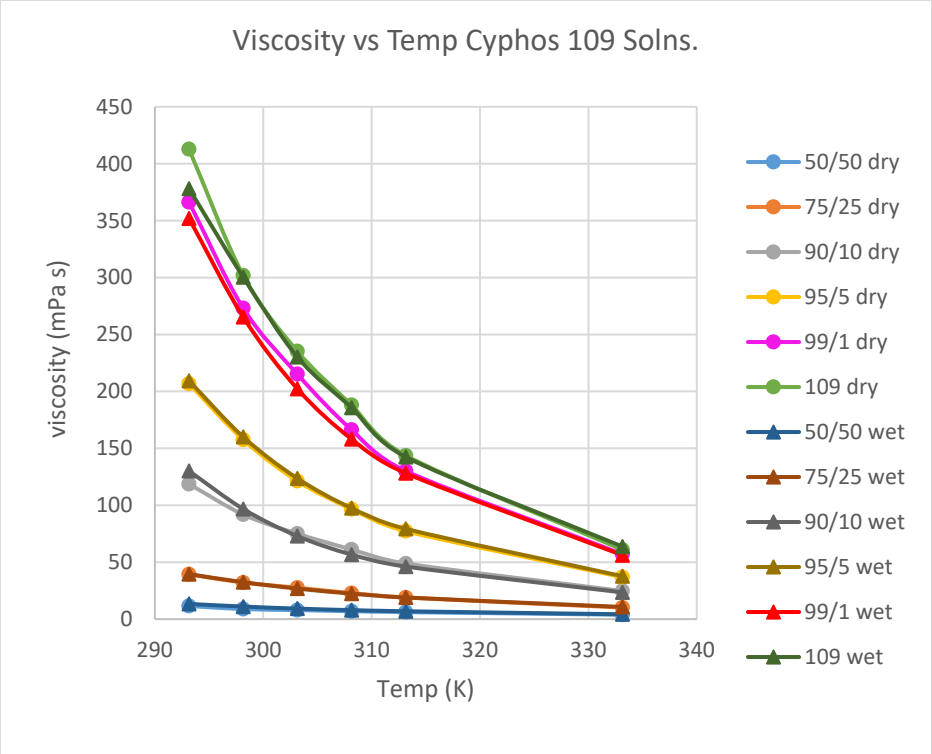

Figure 3b. Plot of the Viscosity vs Temp. for Cyphos 109 solutions

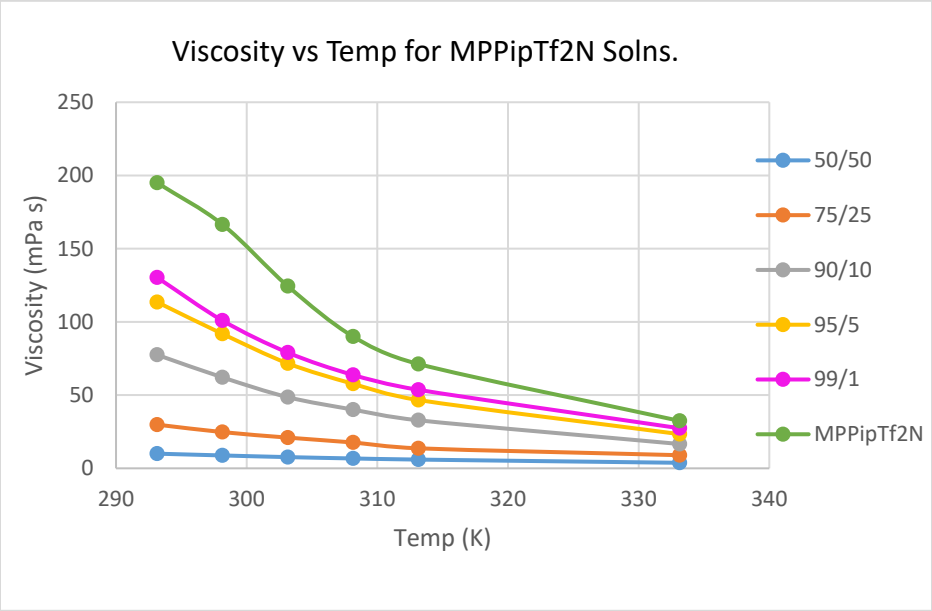

Figure 3c. Plot of the Viscosity vs Temp. for MPPipTf2N solutions

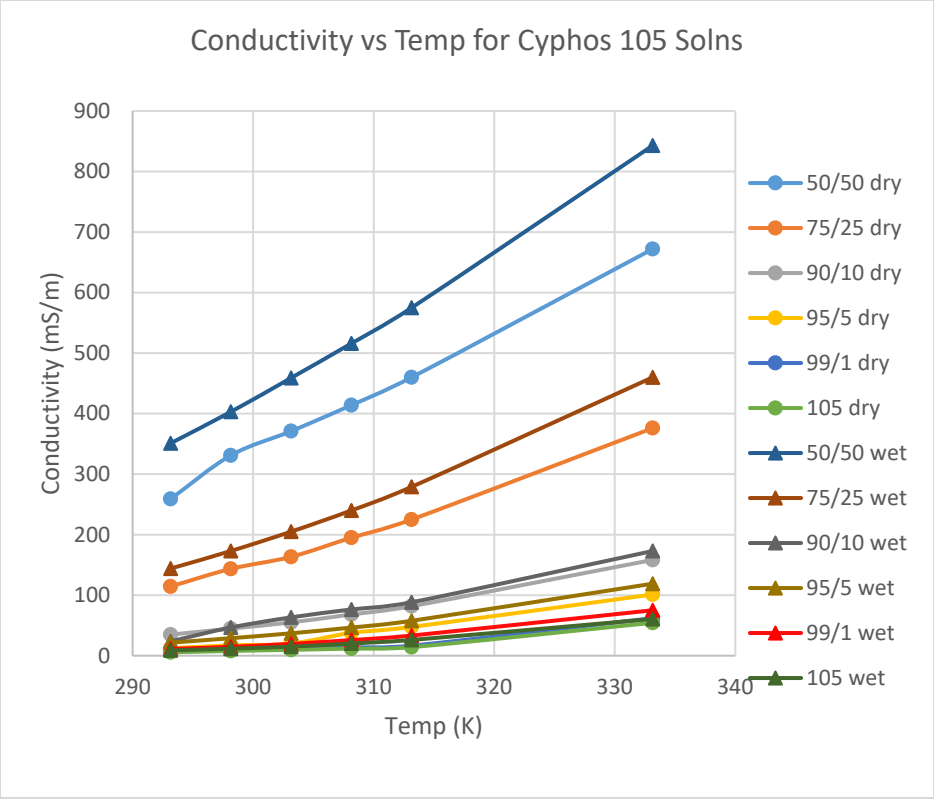

Figure 4a. Plot of the Conductivity vs Temp. for Cyphos 105 solutions

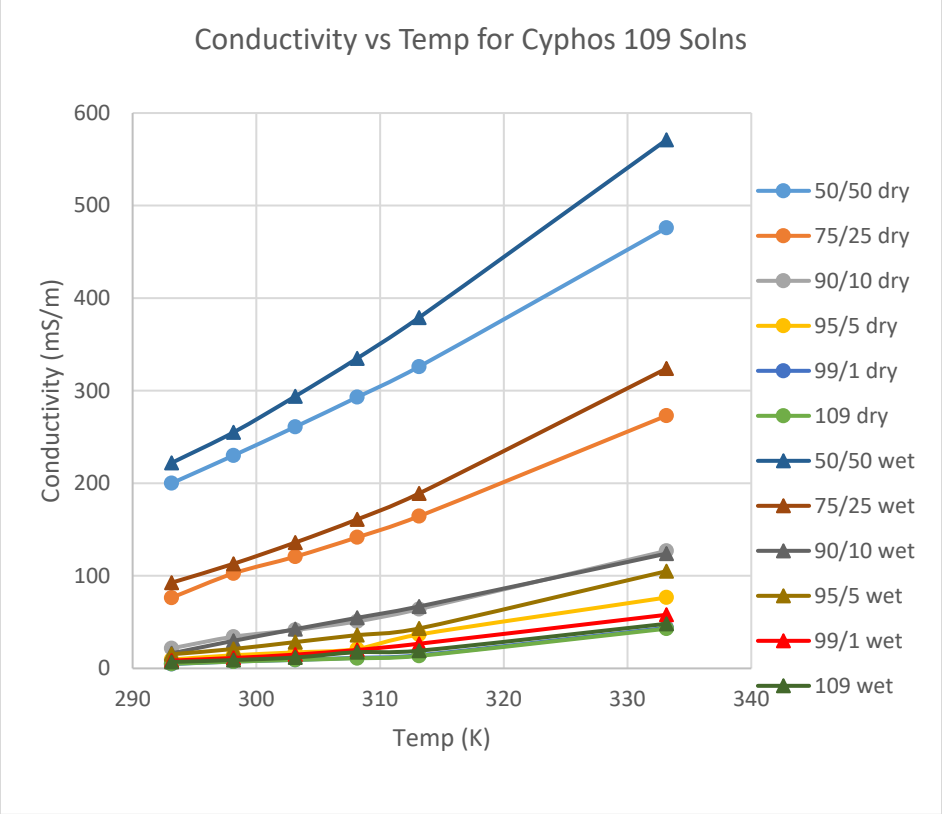

Figure 4b. Plot of the Conductivity vs Temp. for Cyphos 109 solutions

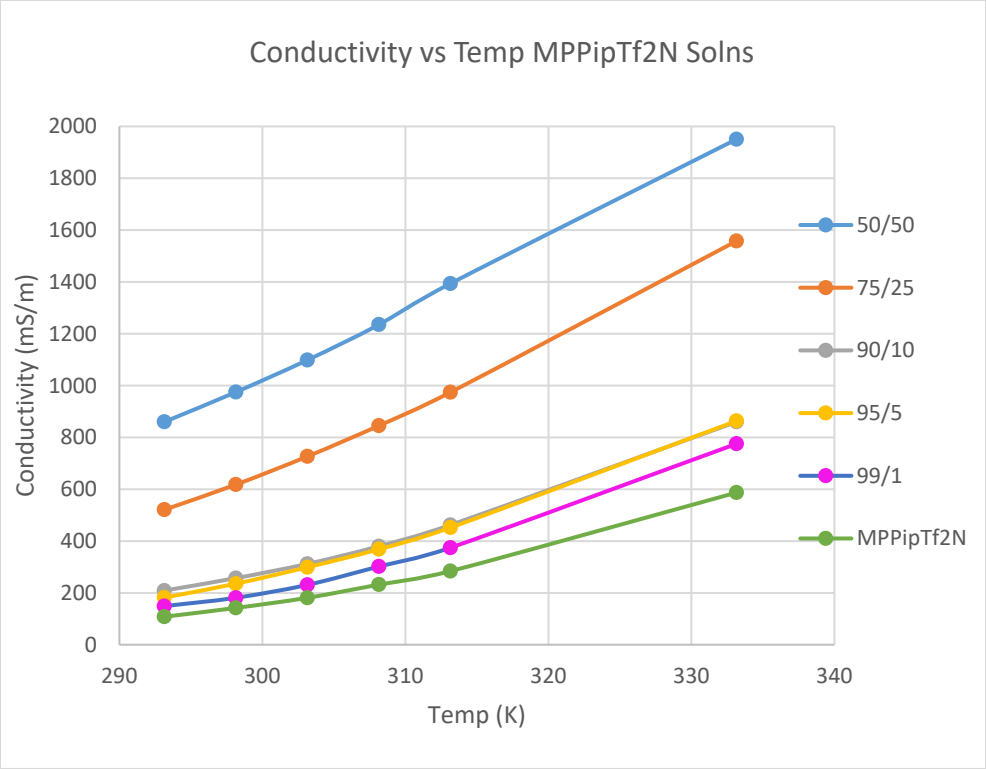

Figure 4c. Plot of the Conductivity vs Temp. for Cyphos 109 solutions

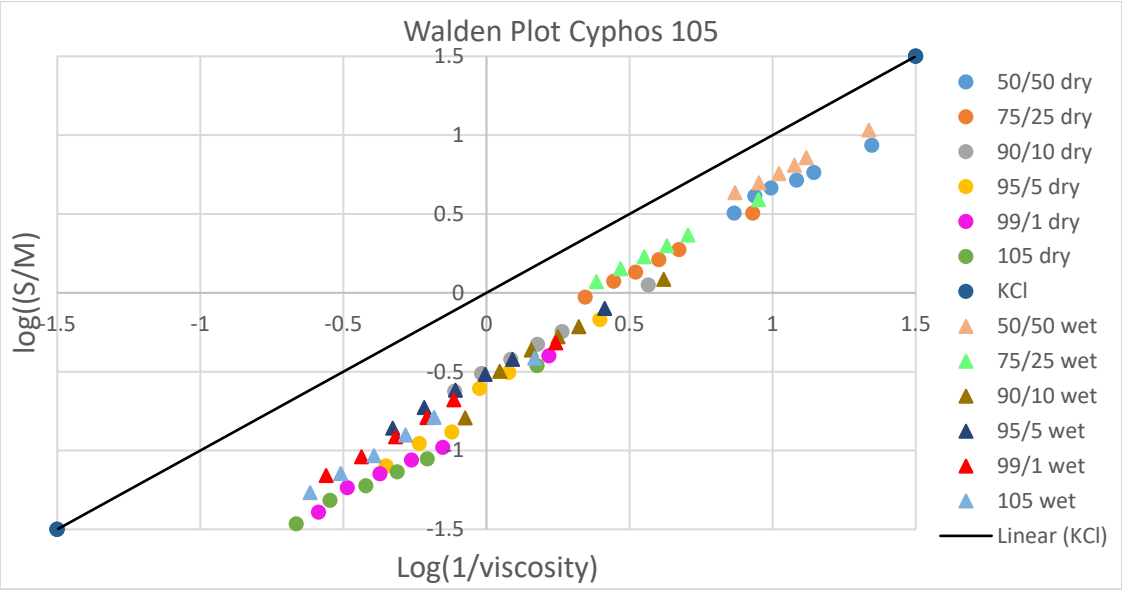

Figure 5a. Walden Plot of Cyphos 105 ionic liquid and solutions in PC at 293, 298, 303, 308, 313, and 333 K.

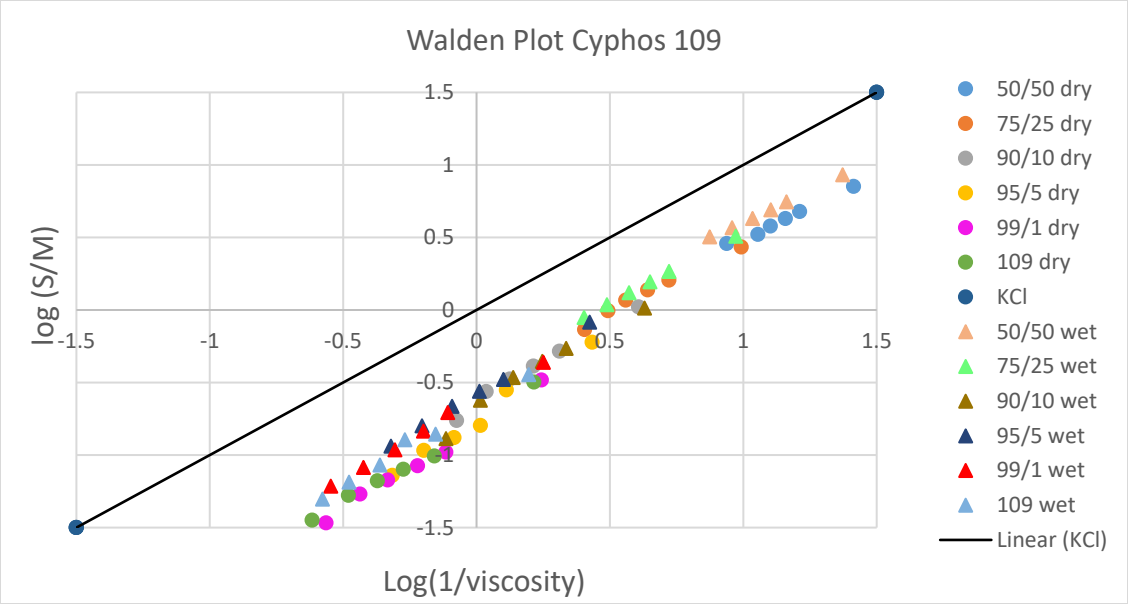

Figure 5b. Walden Plot of Cyphos 109 ionic liquid and solutions in PC at 293, 298, 303, 308, 313, and 333 K.

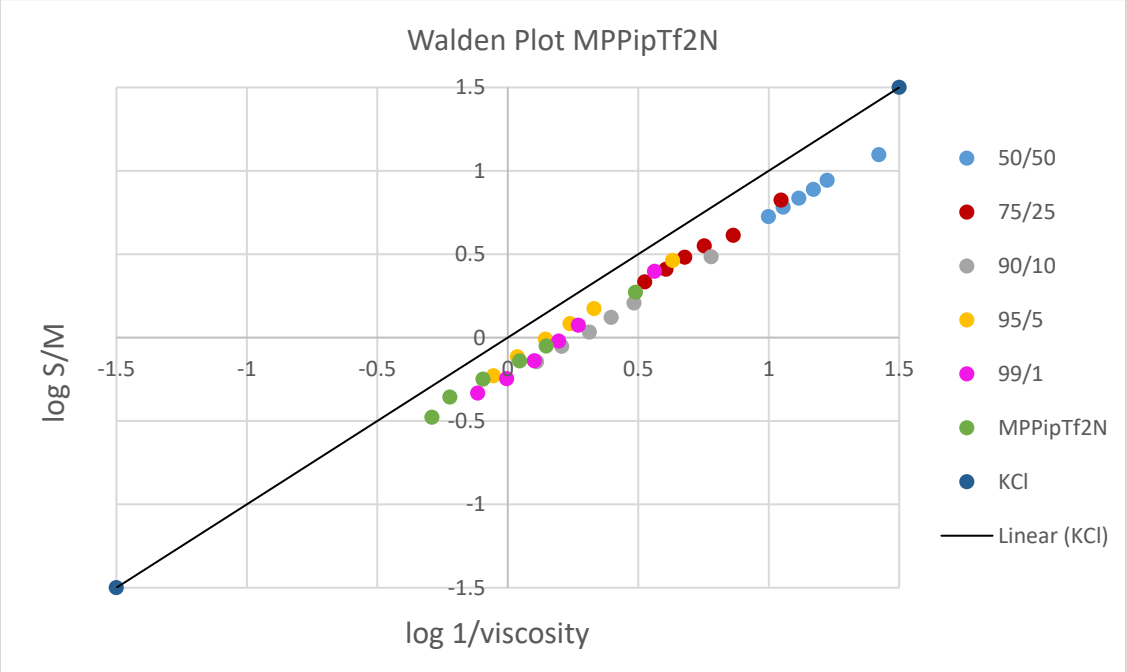

Figure 5c. Walden Plot of MPPipTf2N ionic liquid and solutions in PC at 293, 298, 303, 308, 313, and 333 K.