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Physico-Chemical Properties of Non-Newtonian Shear Thickening Diisopropyl-ethylammonium-Based Protic Ionic Liquids and Their Mixtures with Water and Acetonitrile

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Supporting Information

ABSTRACT: New protic ionic liquids (PILs) based on the diisopropyl-ethylammonium cation have been synthesized through a simple and atom-economic neutralization reaction between the diisopropyl-ethylamine and selected carboxylic acid. Densities and rheological properties were then measured for two original diisopropyl-ethylammonium-based protic ionic liquids (heptanoate and octanoate) at 298.15 K and atmospheric pressure. The effect of the presence of water or acetonitrile on the measured values was also examined over the whole composition range at 298.15 K and atmospheric pressure. From these values, excess properties were calculated and correlated by using a Redlich−Kister-type equation. Finally, a qualitative analysis of the evolution of studied properties with the alkyl chain length of the anion and with the presence or not of water (or acetonitrile) was performed. From this analysis, it appears that selected PILs and their mixtures with water or acetonitrile have a non-Newtonian shear thickening behavior, and the addition of water or acetonitrile on these PILs increases this phenomena by the formation of aggregates in these media.

INTRODUCTION

Ionic liquids are fluids constituted only by ions that have, generally, melting points close to room temperature. Ionic liquids are considered as promising solvents for sustainable chemistry due to their negligible vapor pressure and high thermal stability.[1,2] The properties of ionic liquids can be adjusted by appropriately combining different cations or anions or by introducing different chemical functions in the structure of the ions.[3−6] It is then possible to synthesize task-specific ionic liquids, adequate to the selective solvation of specific chemical families or certain gases.[7−9] Knowledge of the physical-chemical properties, like the density, viscosity, conductivity, or thermal stability, of the different ionic liquids is essential for the development of new industrial processes.[10,11] To date, many references are available in the literature for the aprotic ionic liquids (denoted AILs) subgroup even if relative to the number of AIL combinations few reliable data are available concerning these properties,[4−6,12] as they are strongly dependent on the purity of the samples.[13−15] However, to date, the protic ionic liquids subgroup, which is defined when the selected IL is formed by the transfer of a proton between a Brønsted acid and a Brønsted base, has not received a particularly large share of the literature based on IL studies.[16] Nevertheless, this IL family has many useful properties and potential applications, often arising from their protic nature, including as self-assembly media,[17] reaction media and catalysts for organic reactions,[18] biological applications,[19] proton conducting electrolytes for polymer membrane fuel cells,[20] and explosives.[21]

Prior to developing any industrial applications using ILs, knowledge of their properties in aqueous or nonaqueous solutions is essential.[11] For this reason, many studies, which deal with the behavior of thermodynamic properties of mixtures containing IL with common organic solvent, are available in the literature.[3−6] Many efforts in this field have been devoted to the study of (IL + water) and (IL + alcohol) binary systems, mainly motivated by solubility of ILs in these molecular solvents as well as low environmental impact of these mixtures.[22−35] However, generally, these studies are basically focused on the AILs subgroup and most particularly on imidazolium-based ILs.[36] However, due to the enormous number of possible binary systems, a lot of work remains to be done and most intensely for the PILs subgroup. Our group has already studied the thermodynamic properties of several PILs as pyrrolidinium,[37] morpholinium,[38] ammonium,[39,40] and imidazolium[41] based PILs and their mixtures with other fluids. This present work is the continuation of our work for new PILs based on the diisopropyl-ethylammonium cation. The heptanoate and octanoate anions have been selected for their relatively good micellar properties as already reported by our group in the case of imidazolium-based PIL systems elsewhere.[41]

We present herein volumetric and rheological properties for two original diisopropyl-ethylammonium-based protic ionic liquids at 298.15 K and atmospheric pressure. Furthermore, the effect of the presence of water or acetonitrile on the measured properties was also examined over the whole composition range at 298.15 K and atmospheric pressure. From these values, excess properties were calculated and correlated by using a Redlich−Kister-type equation. Generally, ILs are described in the literature as Newtonian fluids.[42−45] Nevertheless, non-Newtonian behaviors have already been reported for some AILs[46−48] and

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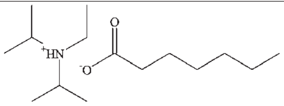
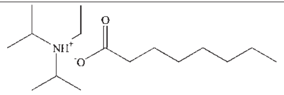
Table 1. Names, Abbreviations, Structures, Molar Masses, and Thermal Stabilities, T_d, of Selected Protic Ionic Liquids at 298.15 K

PILs	Abbreviations	Structures	$\frac{M}{\mathrm{g \cdot mol^{-1}}}$	$\frac{T_d}{\mathrm{K}}$
diisopropyl-ethylammonium heptanoate	[DIPEA][C_6COO]		259.43	397
diisopropyl-ethylammonium octanoate	[DIPEA][C_7COO]		273.45	400

most recently for PILs.[49,50] Non-Newtonian shear thinning phenomena have recently been described in several PILs by Burrell et al.[50] In this paper, Burrell et al. have also investigated the effect of water on this property, and they showed that by increasing the water concentration the rheological behavior of the (PIL + water) binary system changes from non-Newtonian shear thinning, to Newtonian, to non-Newtonian shear thickening behaviors.[50] More recently, a publication of Guo and Guo reports also that ionic liquid induced structure transition of nonionic wormlike micelles composed of Tween 80 and Brij 30.[51] In this paper, the authors have presented information on the micellar structure changes based on rheology and freeze—fracture images.[51] On the basis of these papers,[49−51] we have also reported herein the rheological study of the selected PILs and mixtures to investigate briefly the rheological behaviors of these PILs, the impact of additions of water or acetonitrile on this property, and the formation of aggregates in these media.

EXPERIMENTAL SECTION

Materials and Methods. Heptanoic acid (≥ 98 %), octanoic acid (≥ 98 %), and diisopropyl-ethylamine (≥ 99 %) used to synthesize selected PILs are commercially available (Sigma-Aldrich) and were used without further purification. ^{1}H NMR spectra of PILs are obtained using a a Bruker 200 MHz spectrometer, with $CDCl_3$ as solvent and TMS as the internal standard.

Double distilled deionized water and acetonitrile (≥ 99 % Sigma-Aldrich) were used for the preparation of binary mixtures. These binary mixtures, containing the PIL and molecular solvent, were prepared by mass with an accuracy of $\pm 1 \cdot 10^{-4}$ g using a Sartorius 1602 MP balance.

The densities of pure components and their mixtures were measured using a pycnometer immerged in a thermostatted bath. The temperature was measured by using a 100 Ω platinum resistance thermometer within an accuracy of ± 0.1 K. Prior to use, the pycnometer was calibrated by using water as reference.[52] From this study, the uncertainty of density measurements did not exceed ± 0.2 %.

A Differential Scanning Calorimeter (Perkin-Elmer DSC6) was used to measure the thermal stability of the pure components. The measuring and reference cells were filled with inert aluminum pans. Pure component stabilities were measured under a N_2 atmosphere with a heating rate of 5 $\mathrm{K \cdot min^{-1}}$.

Rheology behaviors of pure components and their mixtures are determined at 298.15 K using a TA Instruments rheometer (AR 1000) with conical geometry. This instrument was fully automated, and therefore, the shear rate and shear stress were, respectively, automatically fixed and determined. The temperature in the cell was regulated to ± 0.01 K with a solid-state thermostat. Viscosity standard (Brookfield, 12700 mPa·s at 298.15 K) and water were used to calibrate the rheometer. From this study, the uncertainty of viscosity measurements did not exceed ± 1 %. For non-Newtonian shear thickening fluids, zero shear viscosities were then deduced using the Cross-type equation (TA Data Analysis V5.1.42 software) within an uncertainty close to ± 3 %.

Preparations of Protic Ionic Liquids. Diisopropyl-ethylammonium-based protic ionic liquids are obtained as the product of an equimolar reaction between the diisopropyl-ethylamine and correspondent acids (heptanoic and octanoic acids). The amine (100.00 g; 0.774 mol) is introduced in a three-neck round-bottom flask immerged in an ice bath and equipped with a reflux condenser, a dropping funnel to add the acid, and a thermometer to monitor the temperature. Under vigorous stirring, heptanoic acid (100.72 g; 0.774 mol)—or the octanoic acid (111.57 g; 0.774 mol)—is added dropwise to the diisopropyl-ethylamine (during 2 h). For each synthesis, the mixture temperature is maintained at less than 298.15 K during the addition of the acid by using an ice bath. For each preparation, stirring is maintained overnight at ambient temperature, and noncolored and low-viscous liquids are then obtained. The residual acids (heptanoic or octanoic acids) are evaporated under reduced pressure, and the remaining liquids are further dried at 386 K under reduced pressure (0.1 Pa) to obtain desired PILs. Diisopropyl-ethylammonium heptanoate, denoted [DIPEA][C_6COO], and diisopropyl-ethylammonium octanoate, denoted [DIPEA][C_7COO], samples were dried overnight at 353 K under high vacuum (0.1 Pa) prior to use. PILs are then analyzed for water content using coulometric Karl Fischer titration prior to all measurements. The water content of selected PILs, measured after treatment, is close to (50 ± 10) ppm. PILs are then characterized by ^{1}H NMR spectrometry. Names, abbreviations, structures, molar masses, and thermal stabilities of selected PILs are listed in Table 1. ^{1}H NMR and DSC characterizations are presented in the Supporting Information (Figures S1 and S2).

RESULTS AND DISCUSSION

Volumetric Properties of Selected PILs and Mixtures. *Volumetric Properties of Pure Compounds.*

Density Measurements. For the pure AILs, the density values vary typically from (1.05 to 1.64) $\mathrm{g \cdot cm^{-3}}$ at 298.15 K. In addition, the density of AILs is very strongly affected by the nature of the anion, which constitutes the AIL.[4−6] AIL's density depends also on the nature of the cation, and it is also described in the literature that the AIL's density decreases with increasing length of the alkyl chain branched in a cation.[5] In the case of PILs, the nature of the anion also has a large effect; for example, 1-methylimidazolium-based PILs constituted of the lactate or the bis(trifluoromethylsulfonyl)imide anions have a density close to

(1.1230 and 1.3672) g·cm^{-3} at (353.15 and 318.15) K, respectively.[4−6] When increasing the alkyl chain length on the cation, the PIL's density decreases; for example, it was reported that densities of lactate-based PILs constituted of alkylimidazolium cations, denoted $[C_nIm]^+$ with n from (1 to 10), range from (1.1230 to 0.9910) g·cm^{-3} at 298.15 K.[16] Furthermore, a similar trend was observed when increasing the alkyl chain length on the anion; for example, imidazolium- and pyrrolidinium-based PILs having carboxylate anions, denoted $[C_mCOO]^-$ with m from (5 to 8), have densities ranging from (1.0256 to 0.9690) g·cm^{-3} and from (0.9880 to 0.9315) g·cm^{-3} at 298.15 K, respectively.[41]

Density measurements of selected pure liquids were carried out at 298.15 K at 0.1 MPa. The experimental data obtained are reported in Table 2 for all the pure compounds studied. For the PILs studied in this paper, densities are related to the compactness of their structure. When the alkyl chain length on the anion increases, the density decreases: $\rho = 0.8665$ g·cm^{-3} for the [DIPEA][C_6COO], and $\rho = 0.8585$ g·cm^{-3} for the [DIPEA][C_7COO], at 298.15 K. As expected, the densities are closely related to the molar mass of the ions with ILs containing heavy atoms found to be most dense, in general. Such a trend is in good agreement with the variation in density with the PIL structure previously reported. Furthermore, the nature of the cation affects strongly the density of the PILs; for example, heptanoate-based PILs composed with imidazolium,[41] pyrrolidinium,[41] and $[DIPEA]^+$ cations have a density of (1.0037, 0.9721, and 0.8665) g·cm^{-3} at 298.15 K, respectively. In other words, $[DIPEA]^+$-based PILs have a lower density than those composed with traditional cation (like imidazolium or pyrrolidinium) based PILs. From Table 2, it is also reported that selected PILs have a density lower than water and acids used during each synthesis.[52,53] However, selected PILs have density higher than acetonitrile and diisopropyl-ethylamine.[53,54]

Table 2. Densities and Molar Volumes of Selected Liquids at 298.15 K and 0.1 MPa

liquid	ρ/g·cm^{-3}	V_m/cm^3·mol^{-1}
[DIPEA][C_6COO]	0.8665	299.41
[DIPEA][C_7COO]	0.8585	318.54
water[52]	0.9970[a]	18.07
acetonitrile	0.7686	53.41
diisopropyl-ethylamine	0.7420	174.20
heptanoic acid	0.9180	141.82
octanoic acid	0.9100	158.48

[a] Water was used as the reference fluid during the calibration of the pycnometer.

Molar Volumes. Molar volumes of pure compounds are reported in Table 2. Due to the difference of the molar masses, as expected, the molar volumes of PILs are slightly higher than those obtained for water and acetonitrile. As already well described in the literature for AILs and PILs, the molar volumes increase with the alkyl chain length.[15] By comparison of other PIL alkylcarboxylate anions, molar volumes of diisopropyl-ethylammonium-based PILs are higher than imidazolium- and pyrrolidium-based PILs. For example, at 298.15 K heptanoate-based PILs constituted of imidazolium,[41] pyrrolidinium,[41] and diisopropyl-ethylammonium cations have molar volumes of (197.4, 207.1, and 299.4) cm^3·mol^{-1}, respectively.

Effect of Water and Acetonitrile on the PILs Volumetric Properties. To investigate the effect of water and acetonitrile on the volumetric properties of PILs, the densities of the (PIL (i = 1) + solvent (i = 2)) mixture—within PIL is [DIPEA][C_6CO_2] and [DIPEA][C_7CO_2] and solvent is water and acetonitrile—are measured at 298.15 K. Results are listed in Tables 3 and 4 and presented in Figures 1 and 2. Excess molar volumes, V^E, are then calculated according to the following equation

$$V^E = \left[\frac{(x_1M_1 + x_2M_2)}{\rho}\right] - \left[\sum_i x_i\frac{M_i}{\rho_i}\right] \qquad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, the molar mass, and the density of component i, respectively.[55] The uncertainty of excess molar volumes, evaluated by propagation of the errors, is estimated to be 0.001 cm^3·mol^{-1}.

Experimental V^E data of studied mixtures are listed in Tables 3 and 4 with accuracy greater than 0.01 cm^3·mol^{-1}. For each

Table 3. Densities, ρ, Molar Volumes, V_m, and Excess Molar Volumes, V^E, for (PIL (1) + Water (2)) as a Function of the PIL Mole Fraction Composition, x_1, at 298.15 K

([DIPEA][C_6COO] + water)				([DIPEA][C_7COO] + water)			
	ρ	V_m	V^E		ρ	V_m	V^E
x_1	(g·cm^{-3})	(cm^3·mol^{-1})	(cm^3·mol^{-1})	x_1	(g·cm^{-3})	(cm^3·mol^{-1})	(cm^3·mol^{-1})
0	0.9970	18.07	0	0	0.9970	18.07	0
0.0998	0.9663	43.57	−2.57	0.0948	0.9551	44.22	−2.34
0.1980	0.9362	70.30	−3.47	0.1930	0.9273	72.60	−3.47
0.2990	0.9136	98.73	−3.46	0.2908	0.9057	101.92	−3.53
0.4007	0.9003	127.45	−3.34	0.3981	0.8906	134.42	−3.26
0.5007	0.8899	156.09	−2.85	0.5050	0.8774	167.59	−2.24
0.5941	0.8840	182.62	−2.59	0.5846	0.8722	191.87	−1.84
0.6913	0.8772	210.78	−1.77	0.6749	0.8672	219.58	−1.27
0.7896	0.8726	239.11	−1.11	0.7994	0.8629	257.53	−0.74
0.9014	0.8695	271.01	−0.67	0.8600	0.8610	276.09	−0.38
1	0.8665	299.41	0	1	0.8585	318.54	0

Table 4. Densities, ρ, Molar Volumes, V_m, and Excess Molar Volumes, V^E, for (PIL (1) + Acetonitrile (2)) as a Function of the PIL Mole Fraction Composition, x_1, at 298.15 K

([DIPEA][C$_6$COO] + acetonitrile)				([DIPEA][C$_7$COO] + acetonitrile)			
	ρ	V_m	V^E		ρ	V_m	V^E
x_1	($g\cdot cm^{-3}$)	($cm^3\cdot mol^{-1}$)	($cm^3\cdot mol^{-1}$)	x_1	($g\cdot cm^{-3}$)	($cm^3\cdot mol^{-1}$)	($cm^3\cdot mol^{-1}$)
0	0.7686	53.41	0	0	0.7686	53.41	0
0.1016	0.8206	77.07	−1.34	0.0948	0.8152	77.39	−1.16
0.2003	0.8408	100.84	−1.83	0.1930	0.8343	102.98	−1.60
0.3046	0.8497	126.59	−1.75	0.2908	0.8422	129.00	−1.51
0.4020	0.8538	150.89	−1.40	0.3981	0.8473	157.65	−1.30
0.5021	0.8571	175.82	−1.11	0.5050	0.8500	186.39	−0.92
0.6083	0.8598	202.25	−0.81	0.5846	0.8520	207.65	−0.75
0.7050	0.8623	226.17	−0.68	0.6749	0.8533	231.94	−0.41
0.8013	0.8639	250.06	−0.46	0.7994	0.8558	265.08	−0.28
0.9013	0.8654	274.86	−0.27	0.8600	0.8565	281.29	−0.12
1	0.8665	299.41	0	1	0.8585	318.54	0

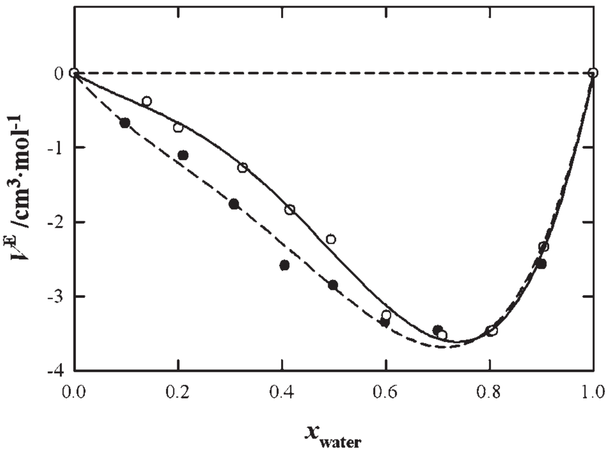


Figure 1. Comparison of excess molar volumes of binary mixtures of (PIL + water) at 298.15 K as a function of water mole fraction composition, x_{water}: ●, [DIPEA][C$_6$COO]; ○, [DIPEA][C$_7$COO]. The lines represent the Redlich−Kister-type fittings with the parameters indicated in Table 5.

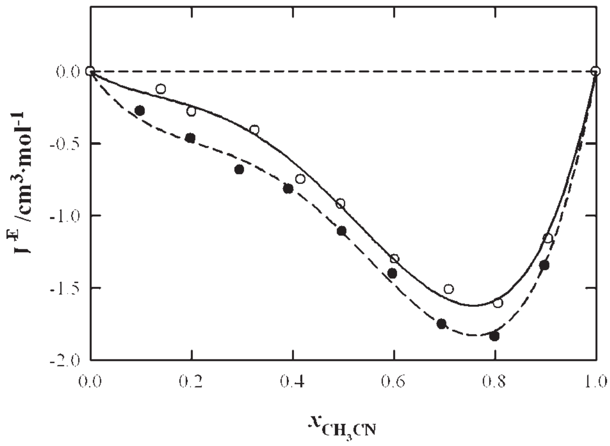


Figure 2. Comparison of excess molar volumes of binary mixtures of (PIL + acetonitrile) at 298.15 K as a function of acetonitrile mole fraction composition, x_{CH3CN}: ●, [DIPEA][C$_6$COO]; ○, [DIPEA][C$_7$COO]. The lines represent the Redlich−Kister-type fittings with the parameters indicated in Table 5.

system, this excess property was correlated as a function of the composition by a Redlich−Kister-type equation

$$V^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \qquad (2)$$

where x_1 and x_2 are the mole fractions of the PIL and the solvent, respectively. The coefficients A_i (with i = 0 to 2) are presented in Table 5 along with the percent relative absolute deviation (100·RAD) between the fitted and experimental excess molar volumes

$$\mathrm{RAD} = \frac{1}{N}\sum \frac{V^E_{calcd} - V^E_{exptl}}{V^E_{exptl}} \qquad (3)$$

where N is the total number of data used; V^E_{calcd} is the excess molar volume calculated from the Redlich−Kister-type eq 2; and V^E_{exptl} is the corresponding value obtained from experimental work reported previously.

Figures 1 and 2 show negative excess molar volumes over the entire mole fraction range for PIL mixtures with water and acetonitrile. Irrespective of the nature of the solvent in studied mixtures or of the sizes of the alkyl chain length in the PILs, all excess molar volumes are limited. For example, extrema are obtained within V^E close to (1.5 to 3.5) cm^3·mol^{-1}, corresponding to (1.5 to 3.3) % of the molar volumes of acetonitrile and water solutions, respectively. Nevertheless, it appears from these figures that the water affects more strongly binary mixtures than the acetonitrile. Furthermore, the increase of the carboxylate alkyl chain length of the PIL from m = 6 to 7 did not affect strongly the excess molar volumes of the solutions. A more peculiar feature of these curves is their asymmetry; in other words, their V^E extrema were localized in the poor region of the PIL mole fraction composition. In the case of acetonitrile PIL solutions, V^E extrema are obtained for mole fractions of acetonitrile close to 0.75, whereas for aqueous solutions, these extrema are observed at mole fractions of water of 0.7. In fact, asymmetrical curves of V^E are more likely to occur when the two components of the mixture have a large molar volume difference, as is indeed the case for water or acetonitrile. It is known that in

Table 5. Redlich−Kister Fitting Coefficients A_i and the Relative Absolute Deviation (RAD) of the Excess Molar Volumes, V^E, of (PIL + Molecular Solvent) Binary Mixtures As a Function of the Molecular Solvent Mole Fraction Composition at 298.15 K

PIL	molecular solvent	A_0	A_1	A_2	100·RAD
[DIPEA][C_6COO]	water	−11.515	−11.681	−8.4312	4.8
	acetonitrile	−4.4746	−6.8279	−7.3740	5.5
[DIPEA][C_7COO]	water	−9.6967	−14.643	−8.9934	5.4
	acetonitrile	−3.7933	−7.0153	−5.2962	9.8

several binary mixtures containing ionic liquids the locus of maxima/minima in V^E against composition is also away from the equimolar composition.[4,30,33−35] Furthermore, several authors have measured the excess molar volumes of binary mixtures containing (ionic liquid + water) for alkylsulfate,[27,28,31,34] tetrafluoroborate,[31,35] and bis(trifluoromethylsulfonyl)imide[31] based ionic liquids and their results exhibiting asymmetric curves with negative-to-positive trends, depending on the nature of ions constituting the ionic liquid. In the case of mixtures containing an AIL as the 1-butyl-3-methylimidazolium hexafluorophosphate, [C_4mim][PF_6], or the 1-butyl-3-methylimidazolium tetrafluoroborate, [C_4mim][BF_4], with acetonitrile, negative excess molar volumes were also reported in the literature.[4] For example, this result was reported by Zafarani-Moattar and Shekaari for the system ([C_4mim][PF_6] + CH_3CN) studied from (298 to 318) K[22] and by Wang et al. for the system ([C_4mim][BF_4] + CH_3CN) studied at 298 K.[23] In both cases, minimum values of the excess molar volumes were obtained for mole fractions of acetonitrile close to 0.7, as reported herein. Nevertheless, at 298 K, the V^E values were less negative than those obtained in this work: − 1.296 $cm^3 \cdot mol^{-1}$ for ([C_4mim][PF_6] + CH_3CN) and −1.122 $cm^3 \cdot mol^{-1}$ for ([C_4mim][BF_4] + CH_3CN).[22,23]

The excess molar volume, V^E, depends mainly on two factors: (i) variation in intermolecular forces between two components in contact and (ii) variation in molecular packing as a consequence of differences in size and shape of molecules. If interactions between unlike molecules are weaker than those between like molecules, excess molar volumes will be positive. For the two selected solvents, the interactions between unlike molecules are higher than those between like molecules as a consequence of negative V^E. Furthermore, V^E diminished with the increase of the anion alkyl chain length is observed, and this effect may be explained by the increase of the apolar part on the anion.

Rheological Properties of Selected PILs and Mixtures. *Rheological Properties of Pure Compounds.* Generally, ILs are described as Newtonian fluids; in other words, their viscosities remain constant with increasing shear rates.[4,6,42,44] For example, Newtonian behaviors for alkylimidazolium (with the alkyl chain length between 1 and 8 carbon atoms) based ILs with tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide anions are reported in the literature.[5,42,44,46−48] Nevertheless, this rheological behavior is strongly affected by the choice of ions constituting the IL. In fact, non-Newtonian behavior has been described for several AILs and PILs.[46−50] For example, Seddon et al.[46] have shown that the alkylimidazolium tetrafluoroborate family (number of carbon atoms is typically 12) is thixotropic fluids whose viscosity decreases when increasing the shear rate. Kulkarni et al.[48] have reported that the flow behavior may change from Newtonian to non-Newtonian by increasing the alkyl chain length on the cation like alkyl-methylimidazolium-based AILs. Non-Newtonian shear thinning behaviors have been then reported for different AILs and recently for PILs.[50]

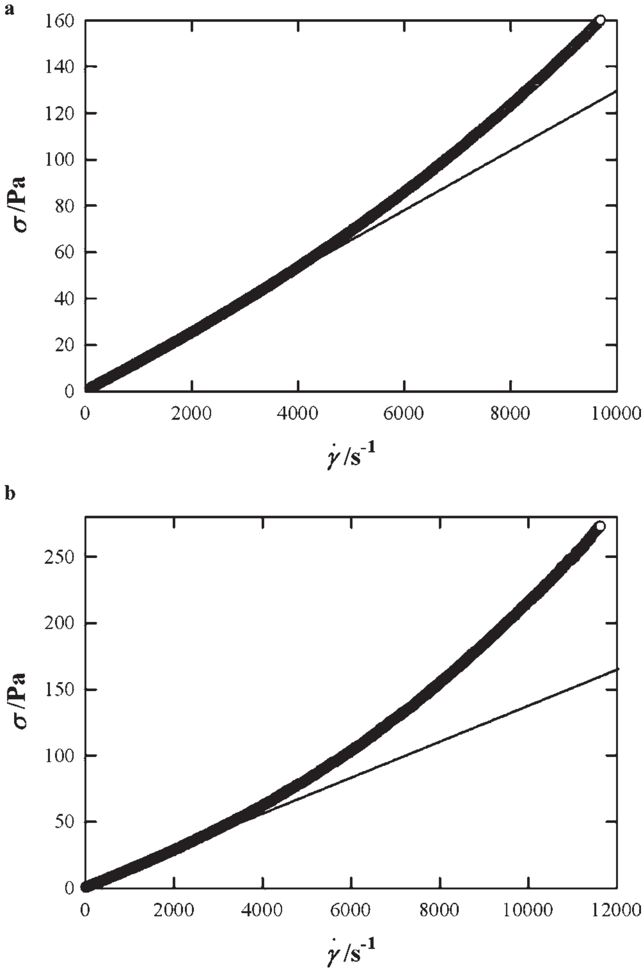


Figure 3. Flow curves for (a) [DIPEA][C_6COO] and (b) [DIPEA][C_7COO] at 298.15 K. The line is just a guide to the eye indicating the deviation from Newtonian behavior.

For the PILs studied, we have first observed a nonlinear relationship between the shear stress and the shear rate, which corresponds to a non-Newtonian behavior as reported in Figure 3. Thus, the shear stress increases monotonically with the shear rate until a shear rate close to (5000 and 4000) s^{-1} for [DIPEA][C_6CO_2] and [DIPEA][C_7CO_2], respectively. Higher shear rates led to an increase in the shear stress. This phenomenon is characteristic of non-Newtonian shear thickening behavior. Shear rate values of (5000 and 4000) s^{-1} in the cases of [DIPEA][C_6CO_2] and [DIPEA][C_7CO_2], respectively, correspond to the onset of the shear thickening. In fact, the apparent viscosity, denoted η_{app}, of fluid presenting a non-Newtonian shear thickening behavior increases when increasing the shear rate as shown in the case of [DIPEA][C_6CO_2], and [DIPEA][C_7CO_2] in Figure 4.

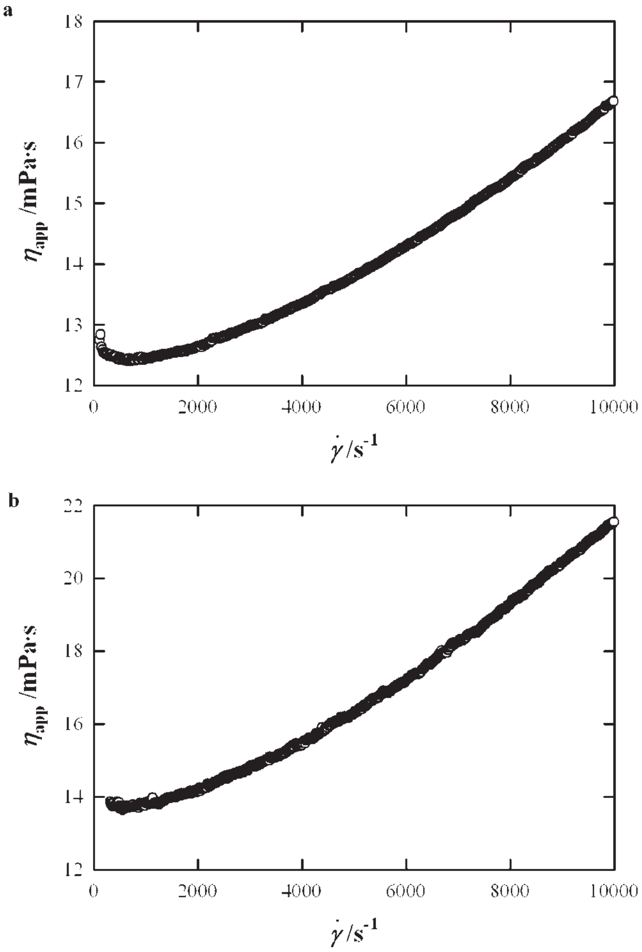


Figure 4. Apparent viscosity as a function of shear rate for (a) [DIPEA][C_6COO] and (b) [DIPEA][C_7COO] at 298.15 K.

Table 6. Zero-Shear Viscosity, η_0, of Studied PILs and Viscosity, η, of Selected Molecular Solvents at 298.15 K

liquid	water	acetonitrile	[DIPEA][C_6COO]	[DIPEA][C_7COO]
η or η_0/mPa·s	0.891	0.335	12.23	13.52

The zero-shear viscosity (denoted η_0) and the viscosity (η) are reported in Table 6 for all the pure compounds studied. For the PILs studied herein, the zero shear viscosity increases when the alkyl chain length on the anion increases: η_0 = 12.23 mPa·s for [DIPEA][C_6COO] and η_0 = 13.52 mPa·s for [DIPEA][C_7COO], at 298.15 K. Such a trend is in good agreement with the variation in viscosity with the PIL structure previously reported.[4−6,16] Furthermore, the nature of ions affects strongly the rheological behavior and in fact the viscosity of the PILs. For example, the pyrrolidinium octanoate-based PIL is Newtonian (at 298.15 K; η = 36.5 mPa·s),[41] but by changing the cation, as reported herein, to the [DIPEA]$^+$ cation, the PIL becomes less viscous but non-Newtonian (at 298.15 K; η_0 = 13.52 mPa·s). Furthermore, Anouti et al.[39,40] have reported Newtonian behaviors in the case of [DIPEA]$^+$-based PILs with formate (at 298.15 K; η = 18.0 mPa·s) and acetate (at 298.15 K; η = 54.4 mPa·s) anions. By comparison with anions studied herein, it appears also that the PIL flow behavior changes from Newtonian to non-Newtonian by increasing the alkyl chain length on the alkylcarboxylate anion.

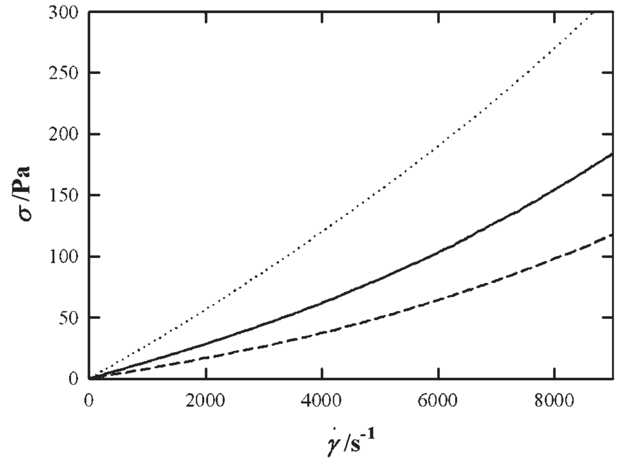


Figure 5. Flow curves for pure [DIPEA][C_7COO] (line) and their equimolar compositions with water (dotted line) and acetonitrile (dashed line) at 298.15 K.

From Table 6, it is noted also that at 298.15 K selected PILs have a zero shear viscosity higher than the viscosities of water and acetonitrile. In other words, studied PILs are more viscous than common molecular solvents. Nevertheless, these PILs are less viscous than traditional AILs, like 1-butyl-3-methylimidazolium tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide, which present viscosities from (50 to 320) mPa·s at 298.15 K[4−6] and have viscosities comparable to other PIL series like alkylmorpholinium formate.[38]

Effect of Water and Acetonitrile on the PIL Rheological Properties. To date, in the literature many authors report that the presence of less viscous fluid (as water or acetonitrile) strongly decreases the viscosity of the IL sample.[13,42] This phenomenon is particularly dramatic in the case of the more viscous IL, as the 1-butyl-3-methylimidazolium hexafluorophosphate.[42] A similar trend was observed in the case of Newtonian and non-Newtonian AILs or PILs. Nevertheless, by increasing the added water in a PIL, presenting originally a non-Newtonian shear thinning behavior, Burrell et al. showed that the flow behavior of the mixture changes from non-Newtonian shear thinning to Newtonian and then from Newtonian to non-Newtonian shear thickening.[49,50] Altin et al.[56] have reported, in the case of the Newtonian IL 1-ethyl-3-methyl ethylsulfate, that depending on the concentration of Fe_2O_3 particles in this IL the flow behavior of the mixture can change also from Newtonian to non-Newtonian shear thinning and shear thickening.

Herein, to investigate the effect of water and acetonitrile on the PIL non-Newtonian behavior, rheological properties of (PIL (i = 1) + solvent (i = 2)) mixtures are measured at 298.15 K. For the studied mixtures, we have first observed, as for pure PILs, a nonlinear relationship between the shear stress and the shear rate corresponding to a non-Newtonian shear thickening behavior as reported in Figure 5 in the case of the [DIPEA][C_7COO] equimolar compositions with water and acetonitrile and in the Supporting Information for each studied binary mixture (see Supporting Information Figures S3 to S6). From these figures, it appears also that for the same value of shear rate the share stress of water binary mixtures is higher than the share stress of pure liquids. In other words, (PIL + water) mixtures are more viscous than pure PILs. A similar trend was observed in the case of binary mixtures containing a low composition of acetonitrile. Zero-shear viscosities of investigated binary mixtures are reported in

Table 7. Zero-Shear Viscosity, η_0, for (PIL (1) + Molecular Solvent (2)) as a Function of the PIL Mole Fraction Composition, x_1, at 298.15 K

	η_0/mPa·s			
x_1	([DIPEA][C_6COO] + water)	([DIPEA][C_6COO] + acetonitrile)	([DIPEA][C_7COO] + water)	([DIPEA][C_7COO] + acetonitrile)
0	0.891	0.335	0.891	0.335
0.1	21.99	1.090	36.61	1.291
0.2	43.71	1.826	52.36	1.947
0.3	41.58	2.510	42.39	2.865
0.4	31.51	3.875	32.19	4.921
0.5	26.92	5.158	27.62	6.897
0.6	23.65	7.013	26.19	8.725
0.7	22.67	9.000	21.29	11.00
0.8	18.07	11.60	18.05	13.31
0.9	14.44	13.50	16.65	14.82
1	12.23	12.23	13.52	13.52

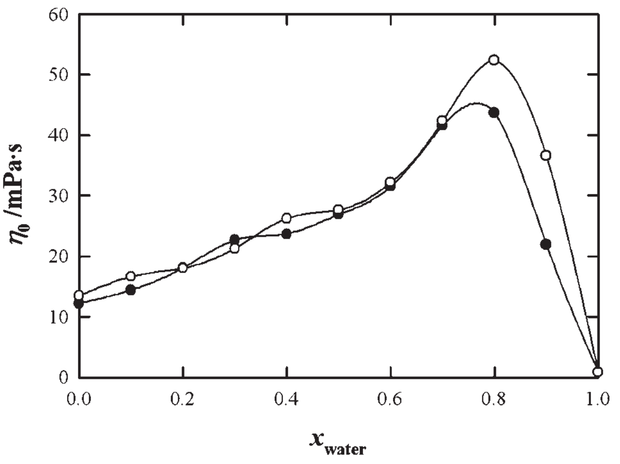


Figure 6. Comparison of zero-shear viscosities, η_0, of binary mixtures of (PIL + water) at 298.15 K as a function of water mole fraction composition, x_{water}: ●, [DIPEA][C_6COO]; ○, [DIPEA][C_7COO]. The lines are just a guide to the eye.

Table 7. Figures 6 and 7 show the variation of the zero-shear viscosity over the entire mole fraction range for PIL mixtures with water and acetonitrile. Irrespective of the solvent in studied mixtures or of the sizes of the alkyl chain length in the PILs, the maximum of zero-shear viscosity is not obtained for a pure liquid. Maxima of zero-shear viscosity are obtained for PIL mole fractions close to (0.2 and 0.9) in the case of binary mixtures containing water and acetonitrile, respectively. It appears also from these figures that the water affects more strongly the rheological behaviors of studied binary mixtures than the acetonitrile. In the case of acetonitrile PIL solutions, zero-shear viscosity maxima are obtained for a PIL mole fraction, x_1 close to 0.9. For this composition, η_0 maxima are close to (13.50 and 14.82) mPa·s in the case of mixtures containing [DIPEA][C_6COO] and [DIPEA][C_7COO], respectively. In the case of water mixtures, η_0 maxima were obtained in a water-rich region, x_1 close to 0.2, within values close to (43.71 and 52.36) mPa·s for mixtures containing [DIPEA][C_6COO] and [DIPEA][C_7COO], respectively. Furthermore, by increasing the carboxylate alkyl chain length of the PIL from m = 6 to 7, the zero-shear viscosity increases.

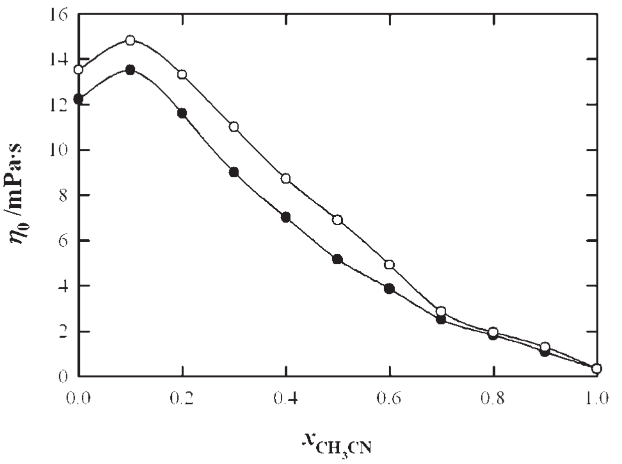


Figure 7. Comparison of zero-shear viscosities, η_0, of binary mixtures of (PIL + acetonitrile) at 298.15 K as a function of acetonitrile mole fraction composition, x_{CH3CN}: ●, [DIPEA][C_6COO]; ○, [DIPEA][C_7COO]. The lines are just a guide to the eye.

The addition of water (acetonitrile) on these PILs induces the non-Newtonian shear thickening behavior observed for each studied PIL. This phenomenon may be due to the formation of aggregates in these media. As the zero-shear viscosity maxima were not obtained for the same solvent-rich region, these reorganizations depend on the nature of the solvent. Zero-shear viscosity maxima were obtained in the PIL-rich region for aprotic solvents like acetonitrile and in the solvent-rich region for protic solvents such as water. In fact, the source of aggregation in non-Newtonian PILs depends strongly on hydrogen bonding. Furthermore, the observed increase of maxima of zero-shear viscosities with the anion alkyl chain length may be explained by the increase of the apolar part on the anion, which may be affected also by the aggregate interaction of these media.

■ CONCLUSION

Heptanoate and octanoate diisopropyl-ethylammonium protic ionic liquids have been prepared by neutralization of the diisopropyl-ethylamine by the corresponding carboxylic acid. Their volumetric properties were then measured at 298.15 K and atmospheric pressure. From these studies, it appears that selected PILs have a lower density than water but higher than acetonitrile. The molar volume of these PILs increases with the alkyl chain length of the carboxylate anion, leading to a less compact structure in the liquid state.

Volumetric properties of binary mixtures containing selected PILs with two molecular solvents (water and acetonitrile) were then studied at 298.15 K. Excess molar volumes for each studied mixture were determined from the experimental data. They exhibit negative deviations from the ideal behavior over the entire range for all investigated (PIL + solvent) systems. In the mean time, rheological properties of pure PILs and their mixtures with water and acetonitrile were then carried out at 298.15 K. Selected PILs and mixtures exhibit non-Newtonian shear thickening behaviors, which depend on the nature of solute and the alkyl chain length of the carboxylate anion. Zero-shear viscosities were then calculated and compared as a function of the nature of the solute, the mixture composition, and the alkyl chain length of the carboxylate anion. Mixtures containing the octanoate-based PIL have higher zero-shear viscosity values than heptanoate solutions. Furthermore, maxima values of the zero-shear viscosities, for water mixtures obtained in the water-rich-region, by comparison with maxima values localized in the PIL-rich region for acetonitrile mixtures, indicate specific interactions and a possible formation of aggregates leading to complex formation through intermolecular hydrogen bonding. A systematic study, involving the size of these aggregates, should aid the understanding of the influence of PILs and solvent structures in the flow behaviors of these solutions and will be presented and discussed in later publications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR and DSC characterizations of studied PILs are shown in Figures S1 and S2. Rheological behaviors of selected PILs against water or acetonitrile concentrations are shown in Figures S3, S4, S5, and S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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