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Physicochemical Properties of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ Ionic Liquids

Ji-Guang Li, Yu-Feng Hu,* Shan Ling, and Jin-Zhu Zhang

State Key Laboratory of Heavy Oil Processing and High Pressure Fluid Phase Behavior & Property Research Laboratory,
China University of Petroleum, Beijing 102249, China

ABSTRACT: The density, viscosity, conductivity, and heat capacity of 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$) and 1-hexyl-3-methylimidazolium tris(perfluoroalkyl)trifluorophosphate ($[C_6mim][(C_2F_5)_3PF_3]$) were measured in the (293.15 to 343.15) K range. According to these experimental and estimated results, the coefficients of thermal expansion and conductivity apparently increase from $[C_6mim][PF_6]$ to $[C_6mim][(C_2F_5)_3PF_3]$, while the crystal energy, the temperature dependence of the heat capacity, and viscosity greatly decrease from $[C_6mim][PF_6]$ to $[C_6mim][(C_2F_5)_3PF_3]$ in the examined temperature range. These comparisons were combined to assess the effect of the replacement of three F atoms of the hexafluorophosphate anion by three hydrophobic C_2F_5-groups on the physicochemical properties of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$.

INTRODUCTION

Ionic liquids (ILs) have been recognized as novel designable solvents, which are liquids over a wide temperature range.[1,2] ILs have unique properties such as negligible vapor pressure, high ion conductivity, outstanding catalytic property, and high thermal stability. One of the most important advantages is that ILs can be tuned by tailoring their cationic and anionic structures to optimize their physical and chemical properties.[1−5]

Recently, a new class of ILs containing tris(perfluoroalkyl) trifluorophosphate (FAP) anions were developed by Merck KGaA as replacements for ILs containing the $[PF_6]^-$ anion.[6,7] One of the most peculiar properties exhibited by these ILs is their strong hydrophobic nature.[8] It has been shown to be a promising means of overcoming the hydrolytic instability of these ILs containing FAP anions[6,9] and is much less than that of ILs containing the bis[(trifluoromethyl)sulfonyl]imide ($[Tf_2N]^-$) anion and more than 10 times less than that of ILs consisting of the $[PF_6]^-$ anion.[6,10] This group of ILs show excellent hydrolytic, thermal, and electrochemical stability, and so on.[6−17] These excellent characteristics make them ideal candidates in synthesis,[11] solvents,[10,12] electrochemistry media,[13] gas absorption, and battery applications.[14−17] Brennecke and co-workers found that the FAP-based ILs possessed higher CO_2 solubility than most other ILs, which was believed to be due to the increased fluoroalkyl chain.[14]

All of these applications clearly indicate that the FAP anion imparts unique attractive characteristics to the IL, so it is important to study the physicochemical properties of FAP-based ionic liquids. Ignat'ev et al. reported conductivity and viscosity of ionic liquids with FAP anions at 293.15 K.[18] Anderson et al. reported viscosities, densities, and surface tensions of four FAP-based ionic liquids at 298.15 K.[10] Liu et al. reported densities and surface tensions of $[C_2mim][(C_2F_5)_3PF_3]$ in the (283.15 to 338.15) K range.[19] Minami et al. reported glass transitions and viscosity at (313.15 and 373.15) K of $[C_nmim][(C_2F_5)_3PF_3]$ ($n = 2, 6, 18$).[20] However, relative few references have been made on a systematic study on the physicochemical properties on FAP-based ionic liquids at different temperatures and compared them to $[PF_6]^-$-based ionic liquids. Furthermore, the conductivities of imidazolium-based ionic liquids at different temperatures are scarce. Therefore, in this paper the density, conductivity, viscosity, and heat capacity were measured for pure $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K range, and they were combined to assess the effect of the replacement of three F atoms of the hexafluorophosphate anion by three hydrophobic C_2F_5-groups on the physicochemical properties of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$.

EXPERIMENTAL DETAILS

Chemicals. $[C_6mim][(C_2F_5)_3PF_3]$ was purchased from Merck with a claimed purity of greater than 0.99. $[C_6mim][PF_6]$ was prepared by well-established procedures described in previous works, with the purity of greater than 0.99.[21,22] The ionic liquids were dried under vacuum over $CaCl_2$ for 2 days at 343 K and were then further dried with 3 Å molecular sieves for several days immediately prior to use. The water content of these ionic liquids after this drying, as measured by Karl Fisher titration, was less than 0.012 mass fraction.

Density. Densities of ionic liquids were measured using a KEM oscillating-tube digital densimeter (DA-505) thermostatted to better than ± 0.01 K as our previous work.[23] The temperature in the measuring cell was monitored with a digital thermometer. The densimeter was calibrated with double-distilled water and dry air. The densities of water at different temperatures were obtained from the literature. The densities of dry air at different temperatures were taken. The uncertainty in density measurements was $\pm 5 \cdot 10^{-5}\ g \cdot cm^{-3}$.

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Viscosity. The viscosity measurement was carried out by a Brookfield DV-I viscometer with a small sample adapter, and the uncertainty was ± 1 %. The temperature was controlled in the range of (293.15 to 343.15) K by a Brookfield TC-502D circulation-type thermo-regulated water bath with a temperature stability of ± 0.1 K. The temperature was held fixed for at least 30 min at each selected temperature to get a more accurate and stable sample temperature.

Conductivity. The conductivity measurements were carried out with a Mettler Toledo SevenEasy conductivity meter calibrated with standard aqueous potassium chloride solutions as our previous work, and the uncertainty was ± 0.5 %.[24] During measurements, the cell was immersed in a model 501A thermostatic bath filled with silicone oil. The bath temperature was kept constant to within ± 0.05 K. The temperature was measured with a Pt100 probe with an evaluating standard uncertainty of ± 0.006 K.

MDSC (Modulated Differential Scanning Calorimeter). The heat capacity was measured with a differential scanning calorimeter (DSC), model TA Q2000, and the uncertainty was within ± 3 %. The method and theory of MDSC have already been presented in numerous publications.[25] For MDSC several types of experiments exist depending on how the parameters underlying heating rate, temperature amplitude, and modulation period $T = 2\pi/\omega$ are chosen. In this study, a heat-iso temperature profile has been applied to measure the heat capacities of the ionic liquids. The MDSC experiments have been carried out with a constant heating rate of 2 K·min^{-1} in an inert atmosphere (N_2 atmosphere) using sealed aluminum pans, a temperature amplitude of ± 0.531 K, and a modulation period of 100 S.

RESULTS AND DISCUSSION

The measured densities, conductivities, and viscosities of pure $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K range are shown in Tables 1 and 2. The results were compared with the values reported in literature,[10,18,26] and the agreements of density and viscosity of $[C_6mim][PF_6]$ at some temperatures and the density, viscosity, and conductivity of $[C_6mim][(C_2F_5)_3PF_3]$ at 293.15 K are good. We must point out that the conductivity of $[C_6mim][PF_6]$ at 295 K[27] is much higher than our conductivity data of $[C_6mim][PF_6]$ at 293.15 K (1.1 mS·cm^{-1} at 295 K vs 0.388 mS·cm^{-1} at 293.15 K). The conductivity of $[C_8mim][PF_6]$ at 295 K[27] is also more than 3 times higher than the literature data at 298.15,[28] which might be due to contaminated water which was involved during measurement making their conductivity[27] higher.

Table 1. Density, Conductivity, and Viscosity of $[C_6mim][PF_6]$ in the (293.15 to 343.15) K Range

T/K	ρ/(g·cm^{-3})		σ/(mS·cm^{-1})	η/(mPa·S)	
	exp.	ref	exp.	exp.	ref 26a
293.15	1.2967	1.2972[26a]	0.388	693.1	705.1
298.15	1.2929	1.2932[26a]	0.543	485.8	496.4
303.15	1.2887	1.2892[26a]	0.74	350.9	356.8
308.15	1.2851	1.2849[26a]	0.992	255.4	
313.15	1.2810	1.2812[26a]	1.301	189.4	197.0
318.15	1.2770	1.2771[26a]	1.683	147.5	
323.15	1.2730	1.2734[26a]	2.12	114.7	117
328.15	1.2691	1.2694[26a]	2.64	91.1	
333.15	1.2652	1.2654[26b]	3.22	73.5	
338.15	1.2612	1.2613[26b]	3.91	60.0	
343.15	1.2570		4.65	49.6	

Table 2. Density, Conductivity, and Viscosity of $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K Range

T/K	ρ/(g·cm^{-3})		σ/(mS·cm^{-1})		η/(mPa·S)	
	exp.	ref 10	exp.	ref 18	exp.	ref 10
293.15	1.5556	1.557	1.303	1.32	114.3	119
298.15	1.5501		1.665		88.2	
303.15	1.5447		2.09		68.4	
308.15	1.5393		2.58		54.1	
313.15	1.5339		3.13		43.2	
318.15	1.5287		3.74		35.1	
323.15	1.5235		4.4		28.9	
328.15	1.518		5.14		24.4	
333.15	1.5126		5.93		20.3	
338.15	1.5072		6.76		17.3	
343.15	1.5018		7.69		14.8	

Experimental values of ln ρ for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ against T were fitted to the following equation:

$$\ln \rho = a + bT \qquad (1)$$

where ρ is the density, T is the absolute temperature, and a and b are fitting parameters. The coefficient of thermal expansion for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$, α_p, is defined by the following equation:

$$\alpha_p = 1/V(\partial V/\partial T)_p = -(\partial \ln \rho/\partial T)_p \qquad (2)$$

where V is the molar volume of pure IL. Then, $\alpha_p = -b = 6.20 \cdot 10^{-4}$ K^{-1} for $[C_6mim][PF_6]$ is obtained from the slope of the fitting line, with a deviation of $4.1 \cdot 10^{-4}$, and $\alpha_p = -b = 7.01 \cdot 10^{-4}$ K^{-1} for $[C_6mim][(C_2F_5)_3PF_3]$ is obtained from the slope of the fitting line, with a deviation of $1.5 \cdot 10^{-4}$. Generally, the practical IL use was under 373.15 K, with a straight line for ln ρ versus T in this temperature range, so the coefficient of thermal expansion for each typical IL could be considered as a constant. The coefficient of thermal expansion for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ is in the common range for typical ILs[29,30] and is much lower than conventional molecular solvents.[31] It can be concluded from the coefficient of thermal expansion of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ ($6.16 \cdot 10^{-4}$ K^{-1} vs $7.01 \cdot 10^{-4}$ K^{-1}) that the volume variation of $[C_6mim][(C_2F_5)_3PF_3]$ is much more temperature-dependent than that of $[C_6mim][PF_6]$ due to the looser package of ionic networks of $[C_6mim][(C_2F_5)_3PF_3]$.

From the values of the densities, the molecular volumes of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$, V_m, were calculated using the following equation:

$$V_m\ (\text{nm}^3) = M/(N \cdot \rho) \qquad (3)$$

where M is molar mass and N is Avogadro's constant; then V_m = 0.4009 nm^3 for $[C_6mim][PF_6]$ and V_m = 0.6559 nm^3 for $[C_6mim][(C_2F_5)_3PF_3]$ at 298.15 K were obtained. Apparently, the molecular volume of $[C_6mim][(C_2F_5)_3PF_3]$ is much larger than that of $[C_6mim][PF_6]$. According to Glasser's theory,[32] crystal energies (U_{POT}) of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ could be calculated as follows:

$$U_{POT}\ (\text{kJ} \cdot \text{mol}^{-1}) = 2(117.3/V_m^{1/3} + 51.9) \qquad (4)$$

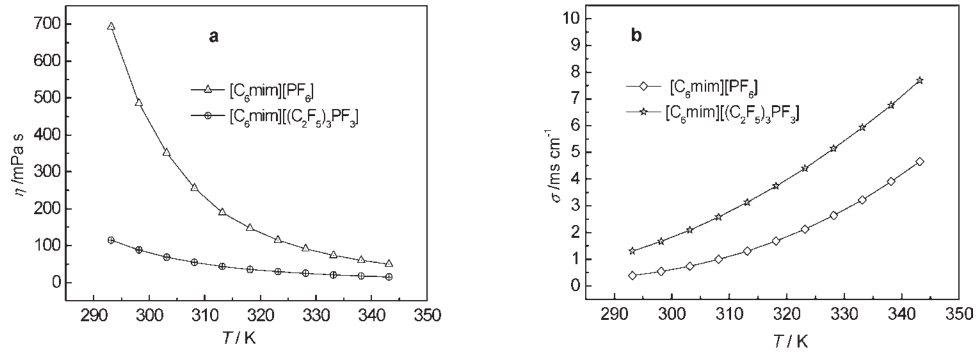

Figure 1. Temperature dependence of (a) viscosities and (b) conductivities of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$.

Table 3. Heat Capacity of $[C_6mim][PF_6]$ in the (293.15 to 343.15) K Range

T	C_p	T	C_p	T	C_p
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
293.15	422	311.15	431	329.15	442
295.15	423	313.15	432	331.15	444
297.15	423	315.15	433	333.15	445
299.15	424	317.15	435	335.15	447
301.15	425	319.15	436	337.15	448
303.15	427	321.15	437	339.15	449
305.15	428	323.15	438	341.15	451
307.15	429	325.15	439	343.15	452
309.15	430	327.15	441		

Table 4. Heat Capacity of $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K Range

T	C_p	T	C_p	T	C_p
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
293.15	726	311.15	742	329.15	757
295.15	727	313.15	743	331.15	759
297.15	729	315.15	745	333.15	760
299.15	731	317.15	747	335.15	761
301.15	732	319.15	749	337.15	763
303.15	734	321.15	750	339.15	765
305.15	736	323.15	752	341.15	766
307.15	738	325.15	753	343.15	768
309.15	740	327.15	755		

Then $U_{POT} = 422\ kJ \cdot mol^{-1}$ for $[C_6mim][PF_6]$ and $U_{POT} = 374\ kJ \cdot mol^{-1}$ for $[C_6mim][(C_2F_5)_3PF_3]$ were estimated at 298.15 K. It is evident that the crystal energy of $[C_6mim][(C_2F_5)_3PF_3]$ is less than that of $[C_6mim][PF_6]$ at room temperature, which means that the ionic network of $[C_6mim][PF_6]$ is more closely packed than that of $[C_6mim][(C_2F_5)_3PF_3]$.

The measured conductivities and viscosities of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K range are illustrated in Figure 1 parts a and b, respectively.

It is clear that the conductivities increase with increasing the temperature, and the viscosities decrease with increasing the temperature for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$. The viscosity greatly decreases from $[C_6mim][PF_6]$ to $[C_6mim][(C_2F_5)_3PF_3]$ in the examined temperature range, with the opposite order for the conductivity, so it can be concluded that the replacement of three F atoms in the $[PF_6]^-$ by three hydrophobic C_2F_5-groups makes $[(C_2F_5)_3PF_3]^-$ a new weakly coordinating anion.

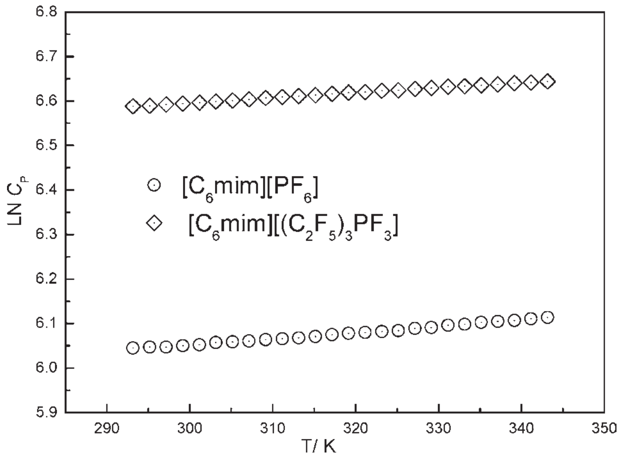

Figure 2. Temperature dependence of ln C_p of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$.

The measured heat capacities of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ in the (293.15 to 343.15) K range are shown in Tables 3 and 4. The heat capacities of $[C_6mim][PF_6]$ were compared with the values reported by Rogers et al.,[33] and the agreements at some temperatures are good. As shown in Figure 2, experimental values of ln C_p for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ against T were fitted to $\ln C_p = a + bT$, respectively, where C_p is heat capacity, T is the absolute temperature, and a and b are fitting parameters.

The temperature dependence of the heat capacity for $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$, μ_p, is defined by

$$\mu_p = 1/C_p(\partial C_p/\partial T)_p = (\partial \ln C_p/\partial T)_p \tag{5}$$

Then, $\mu_p = 1.41 \cdot 10^{-3}\ K^{-1}$ for $[C_6mim][PF_6]$ is obtained from the slope of the fitting line, with the deviation of $1.89 \cdot 10^{-4}$, and $\mu_p = 1.14 \cdot 10^{-3}\ K^{-1}$ for $[C_6mim][(C_2F_5)_3PF_3]$ is obtained from the slope of the fitting line, with the deviation of $2.36 \cdot 10^{-4}$. Although the heat capacity of $[C_6mim][(C_2F_5)_3PF_3]$ is much larger than that of $[C_6mim][PF_6]$, the temperature dependence of the heat capacity follows the order $[C_6mim][PF_6] > [C_6mim][(C_2F_5)_3PF_3]$ due to the looser package of ionic networks of $[C_6mim][(C_2F_5)_3PF_3]$, which agrees with the orders of crystal energy and viscosity $[C_6mim][PF_6] > [C_6mim][(C_2F_5)_3PF_3]$.

CONCLUSIONS

In conclusion, the density, viscosity, conductivity, and heat capacity of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ were measured in the (293.15 to 343.15) K range and at atmospheric pressure in this work. In terms of physicochemical properties of $[C_6mim][PF_6]$ and $[C_6mim][(C_2F_5)_3PF_3]$ and their estimated properties, $[C_6mim][PF_6]$ has a closer package of ionic networks than that of $[C_6mim][(C_2F_5)_3PF_3]$. The replacement of three F atoms of the $[PF_6]^-$ by three hydrophobic C_2F_5-groups makes $[(C_2F_5)_3PF_3]^-$ a new weakly coordinating anion.

It is important to understand how the unique properties of FAP-based ILs differ from those containing other similar anions. The purpose for studying FAP-based ILs is not only for its importance but also for its unique structure, and it can give us a new angle for our further study.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-89732658. E-mail: huyf3581@sina.com.

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