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两种疏水型膦类离子液体的密度、动力粘度及电导率

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摘要: 通过传统的方法, 制备了两种对水和空气稳定的四烷基膦类离子液体。离子液体是: 己基三丁基膦四氟化硼和己基三丁基膦双三氟甲基磺酸亚胺。在 $T = 283.15\text{--}353.15\text{ K}$ 温度范围内, 测定了两个离子液体的密度、动力粘度及电导率。讨论了温度、阴离子结构对离子液体的性质的影响。结合文献报道的其它离子液体, 讨论了该类离子液体性质随阳离子结构的变化规律, 并与咪唑类离子液体的性质进行了比较。通过经验方程, 利用密度数据计算了两个离子液体重要热力学性质参数, 例如: 分子体积、标准摩尔熵及晶格能等。并将估算性质与传统的咪唑、吡啶类离子液体进行了对比。通过密度和电导率确定了离子液体的摩尔电导率。讨论了 Vogel-Fulcher-Tamman (VFT) 方程和 Arrhenius 方程对于粘度和电导率拟合的可行性, 并估算了电导活化能及流动活化能。通过 Walden 规则, 描述了密度、粘度及电导率之间的联系。有关研究对新型离子液体的合成及其工业化的应用具有十分重要意义。

关键词: 离子液体; 密度; 动力粘度; 电导率; Walden 规则

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Density, Dynamic Viscosity and Electrical Conductivity of Two Hydrophobic Phosphonium Ionic Liquids

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Abstract: Two air and water stable hydrophobic phosphonium ionic liquids (ILs), tributyl-hexylphosphonium tetrafluoroborate ([P4446][BF₄]) and tributyl-hexylphosphonium bis(trifluoromethylsulfonyl)imide ([P4446][NTf₂]), were prepared by the traditional method. Their basic physico-chemical properties of density, dynamic viscosity, and electrical conductivity were measured in the temperature range of 283.15–353.15 K. The effect of the temperature and structure of the anion on the thermodynamic properties were discussed. The properties are compared with the cation structures changing of the phosphonium type ILs. The most important thermodynamic properties for their practical application, such as molecular volume, standard molar entropy, and lattice energy, were calculated from their density using empirical equations. The calculated values were compared with those of imidazolium and pyridinium type ILs. Molar electrical conductivity was determined from density and electrical conductivity. The applicability of the Vogel-Fulcher-Tamman (VFT) and Arrhenius equations to the fitting of the dynamic viscosity and electrical conductivity was validated. The activation of the electrical conductivity and

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dynamic viscosity were obtained from the final VFT equation. According to the Walden rule, the density, dynamic viscosity, and electrical conductivity were described by the Walden equation. The results are very important for academic studies as well as industrial applications of these ILs.

Key Words: Ionic liquids; Density; Dynamic viscosity; Electrical conductivity; Walden rule

1 Introduction

The use of ionic liquids (ILs) as green solvents has received much attention because of their physico-chemical properties^{1–4}. ILs commonly exhibit low melting temperatures, good solvation, negligible vapor pressure, high electrical conductivity, good thermal stability, and good designability, among other factors.

As a recent example, tetra(alkyl) phosphonium ionic liquids (TAPILs), with a stable cation, have been synthesized and systematically applied to different areas. These TAPILs commonly exhibit low density, low electrical conductivity, high dynamic viscosity, high thermal stability, and high electrochemical stability^{5,6}. TAPILs with strong nucleophilic anions are significantly more stable than the analogous tetra-alkyl ammonium type ILs⁷. Because of the high dynamic viscosity, TAPILs are also used as the stationary phases for gas chromatography^{8,9}. Many TAPILs exhibit a unique phase behavior with water by increasing or decreasing the temperature, and the mixing of water and TAPILs shows the lowers critical solution temperature (LCST)^{10–12}. In addition to temperature, CO₂ and N₂ can also be used to reversibly change the phase from homogeneous to separated liquid-liquid¹³. TAPILs have also been used for the absorption of CO₂ and SO₂, where CO₂ can be captured by tuning the basicity of the TAPIL¹⁴, and multiple-site absorption can be used for SO₂ capture in the anion of several azole-based TAPILs¹⁵. Although such TAPILs have exhibited outstanding properties, the basis for these properties is relatively unknown, which has prohibited the synthesis and application of new TAPILs. The properties of trihexyl (tetradecyl)phosphonium type ILs have also been studied as examples of common TAPILs^{16–18}. However, such cation TAPILs exhibit greater molecular volumes and higher dynamic viscosities than do more common ILs^{19–29}.

Recently, Tsunashima *et al.*⁶ studied the physical and electrochemical properties of some quaternary phosphonium cation ILs with tetrafluoroborate and bis(trifluoromethylsulfonyl)imide anions included in this type of IL. These two types of anion IL include tributyl(octyl)phosphonium tetrafluoroborate ([P4448][BF₄]), tributyl(dodecyl)phosphonium tetrafluoroborate ([P444(12)][BF₄]), tributyl(octyl)phosphonium bis(trifluoromethylsulfonyl)imide ([P4448][NTf₂]), and tributyl(dodecyl)phosphonium bis(trifluoromethylsulfonyl)imide ([P444(12)][NTf₂]). According to common experience, the influence of the alkyl chain length on the IL properties is clear. In this work, two TAPILs, [P4446][BF₄] and [P4446][NTf₂], were prepared for study by an ion exchange method to further understand this type of TAPIL. The two TAPILs have lower molecular volumes and lower dynamic viscosities relative to trihexyl(tetradecyl)phosphonium type

ILs. The density, dynamic viscosity, and electrical conductivity were probed over the temperature range from (283.15 ± 0.05) to (353.15 ± 0.05) K. The influences of the anion and of methylene introduction on the properties are discussed. Other IL properties are also predicted based on empirical values from previous experiment. These predicted values include density, standard molar entropy, and lattice energy. The values are also compared with literature values⁶. The work provides information on the influence of the anion to the properties after probing of the basic properties of these systems.

2 Experimental

2.1 Materials

Ethyl acetate (Beijing Yili Chemical Reagent Co., China), acetonitrile (Tianjin Tianhe Chemical Reagent Co., China), sodium tetrafluoroborate (NaBF₄) (Shanghai Zhuorui Chemical Co., China), bis(trifluoromethylsulfonyl)imide lithium salt (LiNTf₂) (Rhodia Co., China), 1-bromohexane (Beijing Yili Chemical Reagent Co., China), and tri-*n*-butylphosphine (Shandong Weitian Chemical Reagent Co., China) were used in the synthesis process. All provenance and mass fraction purities of the used materials are listed in Table 1.

2.2 Preparation of TAPILs [P4446][BF₄] and [P4446][NTf₂]

TAPILs [P4446][BF₄] and [P4446][NTf₂] were synthesized by methods described elsewhere^{30,31}. Tributyl(hexyl)phosphonium bromide ([P4446][Br]) was first synthesized. A slight excess of 1-bromohexane was added dropwise into tributylphosphine with stirring at 353 K for 24 h. The white product, [P4446][Br], was recrystallized from an ethyl acetate and acetonitrile solution (the ratio of the volume being 1 : 1) several times. The white product was dried in high vacuum for 48 h at 353 K before the final product synthesis was carried out.

The hydrophobic TAPILs [P4446][BF₄] and [P4446][NTf₂] were synthesized by ion exchange in a distilled water/dichloromethane system. The white product [P4446][Br] was placed in a

Table 1 Provenance and mass fraction purity of the used materials

Chemical name	Provenance	CAS No.	Purity
ethyl acetate	Beijing Yili	141-78-6	> 0.99
acetonitrile	Tianjin Tianhe	75-05-8	> 0.99
NaBF ₄	Shanghai Zhuorui	13755-29-8	> 0.99
LiNTf ₂	Rhodia (Franch)	90076-65-6	> 0.99
1-bromohexane	Beijing Yili	111-25-1	> 0.99
tri- <i>n</i> -butylphosphine	Shandong Weitian	998-40-3	> 0.98

flask and dissolved with the distilled water/dichloromethane system. An equivalent amount of NaBF_4 or LiNTf_2 salt, for $[\text{P4446}][\text{BF}_4]$ or $[\text{P4446}][\text{NTf}_2]$, respectively, was added into the system with stirring. The TAPIL and dichloromethane phase was washed with distilled water until no Br^- was present, where the presence was checked using an $\text{AgNO}_3/\text{HNO}_3$ solution. The colorless liquid was obtained and dried (353 K for 48 h) under vacuum after washing. The final product TAPILs were characterized by ^1H NMR spectroscopy. The final mass fraction purities of the TAPILs were estimated from ^1H NMR spectra to be better than 99% (see Figs.S1 and S2 in the Supporting Information). The structures of TAPILs $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$ are presented in Scheme 1.

2.3 Water content

The water content of the TAPILs $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$ was determined by a Cou-Lo Aquamax Karl Fischer Moisture Meter (v.10.06). The water contents of the samples is less than 300×10^{-6} (mass fraction) before and after determination of the system properties.

2.4 Density and dynamic viscosity

An Anton Paar SVM3000 (Anton Paar Shanghai Trading Co. Ltd.) was used for determining the density and dynamic viscosity of the TAPILs $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$. The temperature range of the measurement is from (283.15 ± 0.05) to (353.15 ± 0.05) K per 5 K, and thermal equilibrium was obtained in 30 min. The experimental error was estimated as $\pm 0.0002 \text{ g} \cdot \text{cm}^{-3}$ for the density and the uncertainty was estimated to be $\pm 1\%$ for the dynamic viscosity.

2.5 Electrical conductivity

The electrical conductivities of the TAPILs $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$ were recorded using a MP522 conductivity meter (San Xin Electronic Co.) with a 1 cm^{-1} cell constant. The cell was calibrated using a standard aqueous KCl solution. The data were recorded every 5 K once thermal equilibrium was attained after 30 min from the temperature increase of (283.15 ± 0.05) to (353.15 ± 0.05) K. The uncertainty is estimated to be $\pm 1\%$.

The values of density, dynamic viscosity, and electrical conductivity are listed in Tables 2 and 3.

3 Results and discussion

From Tables 2 and 3, the density and dynamic viscosity can be seen to decrease with an increase temperature, and the electrical conductivity contrasts with the above two properties, where the data significantly increases in value with an increase temperature.

Scheme 1 Structures of TAPILs $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$

Table 2 Experimental values of density, ρ , dynamic viscosity, η , and electrical conductivity, σ , of $[\text{P4446}][\text{BF}_4]$ from 283.15 to 353.15 K at pressure $p = 0.1 \text{ MPa}$

T/K	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$	$\sigma/(\text{mS} \cdot \text{cm}^{-1})$
283.15	1.0130	4909.7	0.0297
288.15	1.0099	3153.5	0.0428
293.15	1.0067	2088.2	0.0639
298.15	1.0036	1415.2	0.0904
303.15	1.0005	982.12	0.1259
308.15	0.9974	696.55	0.1713
313.15	0.9946	504.02	0.2330
318.15	0.9915	371.46	0.3090
323.15	0.9884	278.52	0.4030
328.15	0.9854	212.04	0.5190
333.15	0.9824	163.86	0.6530
338.15	0.9794	128.36	0.8280
343.15	0.9764	101.84	1.0280
348.15	0.9735	81.776	1.2650
353.15	0.9705	66.434	1.5500

ρ : density; η : dynamic viscosity; σ : electrical conductivity. The uncertainty is $\pm 0.0002 \text{ g} \cdot \text{cm}^{-3}$ for density. The uncertainties are $\pm 1\%$ for electrical conductivity and dynamic viscosity. The uncertainty is $\pm 0.05 \text{ K}$ for temperature.

Table 3 Experimental values of density, ρ , dynamic viscosity, η , and electrical conductivity, σ , of $[\text{P4446}][\text{NTf}_2]$ from 283.15 to 353.15 K at $p = 0.1 \text{ MPa}$

T/K	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$	$\sigma/(\text{mS} \cdot \text{cm}^{-1})$
283.15	1.2027	530.84	0.173
288.15	1.1985	379.98	0.238
293.15	1.1943	278.25	0.318
298.15	1.1903	207.71	0.419
303.15	1.1863	157.91	0.545
308.15	1.1823	122.01	0.709
313.15	1.1783	95.748	0.874
318.15	1.1744	76.216	1.089
323.15	1.1704	61.471	1.342
328.15	1.1665	50.185	1.635
333.15	1.1625	41.446	1.952
338.15	1.1586	34.559	2.320
343.15	1.1547	29.108	2.730
348.15	1.1508	24.739	3.200
353.15	1.1469	21.198	3.730

The uncertainty is $\pm 0.0002 \text{ g} \cdot \text{cm}^{-3}$ for density.

The uncertainties are $\pm 1\%$ for electrical conductivity and dynamic viscosity.

The uncertainty is $\pm 0.05 \text{ K}$ for temperature.

At 293.15 K, the densities of $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$ are 1.0067 and $1.1943 \text{ g} \cdot \text{cm}^{-3}$, respectively. Although the value for $[\text{P4446}][\text{NTf}_2]$ is higher than $[\text{P4446}][\text{BF}_4]$, it is much lower than the common IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_4\text{mim}][\text{NTf}_2]$ ($1.4378 \text{ g} \cdot \text{cm}^{-3}$)³².

At 298.15 K, the dynamic viscosity of the $[\text{P4446}][\text{BF}_4]$ and $[\text{P4446}][\text{NTf}_2]$ are 1415.2 and $207.71 \text{ mPa} \cdot \text{s}$, respectively. These values are much higher than for the ILs $[\text{C}_4\text{mim}][\text{BF}_4]$ ($75 \text{ mPa} \cdot \text{s}$) and $[\text{C}_4\text{mim}][\text{NTf}_2]$ ($40 \text{ mPa} \cdot \text{s}$)³³. The electrical conductivities

Table 4 Density, dynamic viscosity, and electrical conductivity of the some tetra-alkyl phosphonium type ionic liquids with literature at 298.15 K

Parameter	Value					
	[P4446][BF ₄]		[P4448][BF ₄]		[P444(12)][BF ₄]	
$\rho/(\text{g}\cdot\text{cm}^{-3})$	1.0036		0.9894 ^a	1.02 ^b	0.9670 ^c	0.97 ^b
$\eta/(\text{mPa}\cdot\text{s})$	1415.2		1240 ^b		1310 ^b	
$\sigma/(\text{mS}\cdot\text{cm}^{-1})$	0.0904		0.069 ^b		0.0468 ^b	
	[P4446][NTf ₂]		[P4448][NTf ₂]		[P444(12)][NTf ₂]	
$\rho/(\text{g}\cdot\text{cm}^{-3})$	1.1903	1.18 ^a	1.1666 ^c	1.18 ^b	1.1276 ^c	1.13 ^b
$\eta/(\text{mPa}\cdot\text{s})$	207.71	261 ^a	250 ^b		303 ^b	
$\sigma/(\text{mS}\cdot\text{cm}^{-1})$	0.419	0.43 ^a	0.268 ^b		0.177 ^b	
					[P666(14)][NTf ₂]	
					1.0654 ^c	
					376.0 ^d	

^aRef.7, ^bRef.6, ^cRef.19, ^dRef.22, ^epredicted value

of [P4446][BF₄] and [P4446][NTf₂] are 0.0904 and 0.419 mS·cm⁻¹, respectively, and these values are much lower than those for ILs [C₄mim][BF₄] (4.5 mS·cm⁻¹) and [C₄mim][NTf₂] (4.6 mS·cm⁻¹)³³.

To compare the density, dynamic viscosity, and electrical conductivity of the tetra(alkyl)phosphonium type ionic liquids with reported literature values^{6,7,19,22}, the above property values of the TAPILs determined at 298.15 K are listed in Table 4. The TAPIL anions are [BF₄⁻] and [NTf₂⁻].

From Table 3, the values at 298.15 K of density, dynamic viscosity, and electrical conductivity of [P4446][NTf₂] are 1.1903 g·cm⁻³, 207.71 mPa·s, and 0.419 mS·cm⁻¹, respectively. At the same temperature, the values of the reference are 1.18 g·cm⁻³, 261 mPa·s, and 0.43 mS·cm⁻¹, respectively⁷. From the literature⁷, the density, dynamic viscosity, and electrical conductivity values were measured by a precalibrated pycnometer, slow-flow viscometer, and ThermoOrion conductivity meter, respectively. The primary reasons for discrepancies with the literature values are the water content, instrumentation used, and purity of the [P4446][NTf₂].

3.1 Density

The temperature dependence on the density can be plotted (see Fig.1) and fitted over the temperature range from (283.15 ± 0.05) to (353.15 ± 0.05) K by the following equation:

$$Y = A + BT \quad (1)$$

where Y is the density; and A and B are adjustable parameters. The fitting equations are obtained from $Y = 1.1844 - 6.06 \times 10^{-4} T$ for [P4446][BF₄] and $Y = 1.4273 - 7.95 \times 10^{-4} T$ for [P4446][NTf₂]. The correlation coefficients of the two TAPILs are 0.9999, which indicates that the linear equation represents the density very well.

The temperature dependence on $\ln\rho$ can be fitted by the following linear equation:

$$\ln\rho = b - \alpha T \quad (2)$$

where b is an empirical constant and α is the thermal expansion coefficient. The fitting equations are $\ln\rho = 0.1860 - 6.11 \times 10^{-4} T$ for [P4446][BF₄], and $\ln\rho = 0.3760 - 6.77 \times 10^{-4} T$ for [P4446][NTf₂]. The correlation coefficients are higher than 0.9999 for both cases, thus indicating that the empirical linear equation represents the density very well. From Equation (2), the thermal expansion coefficients are 6.11×10^{-4} for [P4446][BF₄] and 6.77×10^{-4} for

[P4446][NTf₂]. These values are in good agreement with the values reported by Jacquemin *et al.*³⁴ that ranged between 5×10^{-4} and $7 \times 10^{-4} \text{ K}^{-1}$ (at 293.15 K, [Bmim][NTf₂] are 6.51×10^{-4} and $6.90 \times 10^{-4} \text{ K}^{-1}$ at dried and saturated, respectively; like: [Bmim][BF₄] is 5.95×10^{-4} at dried). The thermal expansion coefficients of the two TAPILs at 298.15 K are listed in Table 5.

At 298.15 K, the molecular volume, V_m , standard molar entropy, S^0 , and lattice energy, U_{pot} , were calculated for the TAPILs [P4446][BF₄] and [P4446][NTf₂] by the traditional empirical equations from the density³²:

$$V_m = M/(\rho N) \quad (3)$$

$$S^0 = 1246.5 V_m + 29.5 \quad (4)$$

$$U_{\text{pot}} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (5)$$

where M is the molar mass, ρ is the density, and N is Avogadro's constant. The obtained data from the above equations are listed in Table 5.

From Table 5, the lattice energy values are 379.0 kJ·mol⁻¹ for [P4446][BF₄] and 357.4 kJ·mol⁻¹ for [P4446][NTf₂]. These values are much lower than for traditional organic melt salts. For example, the lowest lattice energy among the alkali halides is for fused CsI (613 kJ·mol⁻¹)³⁵. The lower lattice energy may be a reason why the two TAPILs have relatively low melting temperatures, such that [P4446][BF₄] and [P4446][NTf₂] can exist in the liquid state at room temperature.

From Table 5, the molecular volumes are 0.6195 nm³ for [P4446][BF₄] and 0.7922 nm³ for [P4446][NTf₂]. These values

Fig.1 Plots of density vs temperature of two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

Table 5 Estimated values of physicochemical properties of two TAPILs [P4446][BF₄] and [P4446][NTf₂] at 298.15 K

Parameter	Value	
	[P4446][BF ₄]	[P4446][NTf ₂]
$M/(\text{g} \cdot \text{mol}^{-1})$	374.29	567.63
V_m/nm^3	0.6195	0.7922
$10^4\alpha/\text{K}^{-1}$	6.11	6.77
$V/(\text{cm}^{-3} \cdot \text{mol}^{-1})$	372.9	476.9
$S^0/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	801.7	1016.9
$U_{\text{pot}}/(\text{kJ} \cdot \text{mol}^{-1})$	379.0	357.4

M : molar mass; V_m : molecular volume; α : thermal expansion coefficients;
 V : molar volume; S^0 : standard molar entropy; U_{pot} : lattice energy

are higher than for more common ILs, e.g., 0.5320 nm³ for [C₆py][NTf₂]³¹, 0.5593 nm³ for [C₆3mpy][NTf₂]³⁶, 0.5633 nm³ for [C₆4mpy][NTf₂]³⁶, 0.5406 nm³ for [C₆Mim][NTf₂]³⁷, and 0.5608 nm³ for [C₆DMim][NTf₂]³⁷.

According to previous reports, the mean contributions of the methylene group to the molecular volume are 0.0277 nm³ for [C_n3mpy][NTf₂]^{36,38}, 0.0289 nm³ for [C_n4mpy][NTf₂]^{38,39}, 0.0280 nm³ for [C_npy][NTf₂]^{31,40}, 0.0282 nm³ for [C_nmim][NTf₂]³², 0.0272 nm³ for [C_nmim][BF₄]³², and 0.0279 nm³ for amino acid ionic liquids^{41–44}. From the literature⁴⁵, the basic properties of 1-alkyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate have been predicted in terms of the estimated molecular volume. In this work, we also predicted the properties of the series of TAPILs based on literature⁴⁵ methods. The mean value of the contribution can be calculated to be 0.0280 nm³. The density, standard entropy, and lattice energy were predicted according to Equations (3)–(5), and the values are listed in Table 6.

From Tables 4 and 6, the predicted density values are agreement with the literature⁶, except for TAPIL [P4448][BF₄]. The comparison, between the values predicted in this work *versus* the

literature shows that the method employed herein is suitable for the prediction of TAPIL properties.

3.2 Electrical conductivity

The molar electrical conductivities of TAPIL [P4446][BF₄] and [P4446][NTf₂] were calculated by the following equation:

$$\Lambda = \sigma M \rho^{-1} \quad (6)$$

where Λ is the molar conductivity, σ is the electrical conductivity, M is the molar mass and ρ is the density. The values of the molar conductivity are listed in Table 7.

The electrical conductivity of the TAPILs [P4446][BF₄] and [P4446][NTf₂] as a function of temperature is plotted in Fig.2. From Fig.2, it can be observed that for each TAPIL the electrical conductivity decreases significantly with an increase in temperature.

Vogel-Fulcher-Tammann (VFT) equations are commonly used for the fitting of temperature dependence to electrical conductivity for ILs. Herein, the temperature dependence of the electrical conductivity for the two TAPILs [P4446][BF₄] and [P4446][NTf₂] were also fitted according to the following VFT equation:

$$\sigma = \sigma_0 \exp(-B/(T - T_0)) \quad (7)$$

where σ is the electrical conductivity; and σ_0 , B , and T_0 are fitting parameters. The fitted parameters of σ_0 , B , and T_0 , and the corresponding correlation coefficient, R , are listed in Table 8. From Table 8, as for other types of IL, the experimental electrical conductivity fits well against temperature by the VFT equation.

The Arrhenius equation is commonly used to fit the electrical conductivity against temperature. However, Vila *et al.*⁴⁶ have shown differing results for ILs, where the electrical conductivity does not always follow Arrhenius behavior with changes in temperature.

The Arrhenius equation is:

$$\sigma = \sigma_\infty \exp(-E_a/(k_B T)) \quad (8)$$

Table 6 Predicted values of the thermodynamic properties of the some tetra-alkyl phosphonium type ionic liquids at 298.15 K

Ionic liquid	$M/(\text{g} \cdot \text{mol}^{-1})$	V_m/nm^3	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$S^0/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$U_{\text{pot}}/(\text{kJ} \cdot \text{mol}^{-1})$
[P4446][BF ₄]	374.29	0.6195	1.0036	801.7	379.0
[P4448][BF ₄]	402.34	0.6755	0.9894	871.5	371.2
[P444(12)][BF ₄]	458.45	0.7875	0.9670	1011.1	357.9
[P4446][NTf ₂]	567.60	0.7922	1.1903	1016.9	357.4
[P4448][NTf ₂]	595.68	0.8482	1.1666	1086.7	351.7
[P444(12)][NTf ₂]	651.79	0.9602	1.1276	1226.3	341.6

Table 7 Molar electrical conductivity, Λ , of two TAPILs [P4446][BF₄] and [P4446][NTf₂] at the temperature from 283.15 to 353.15 K

T/K	[P4446][BF ₄]	[P4446][NTf ₂]	T/K	[P4446][BF ₄]	[P4446][NTf ₂]
283.15	0.011	0.082	323.15	0.153	0.651
288.15	0.016	0.113	328.15	0.197	0.796
293.15	0.024	0.151	333.15	0.249	0.953
298.15	0.034	0.200	338.15	0.316	1.137
303.15	0.047	0.261	343.15	0.394	1.342
308.15	0.064	0.340	348.15	0.486	1.579
313.15	0.088	0.421	353.15	0.598	1.846
318.15	0.117	0.526			

Λ : molar conductivity. The uncertainty is $\pm 1\%$ for molar electrical conductivity. The uncertainty is ± 0.05 K for temperature.

Fig.2 Plots of electrical conductivity vs temperature of two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

$$\ln \sigma = \ln \sigma_{\infty} - (E_{\sigma}/k_B)T^{-1} \quad (9)$$

where E_{σ} is the activation energy, which indicates the energy needed for the ion to hop into a free hole, σ_{∞} is the maximum electrical conductivity and k_B is the Boltzmann constant. From Equation (9), a linear equation, the $1/T$ dependence on $\ln \sigma$ was plotted for the two TAPILs [P4446][BF₄] and [P4446][NTf₂] (see Fig.3).

The plots should be on straight lines but the points clearly show that the experimental points are not on the straight lines (the solid straight lines were drawn to clarify the points). Therefore, the electrical conductivities of the TAPILs also do not follow Arrhenius behavior very well. Similar results were determined by us previously³⁶.

Vila *et al.*⁴⁶ introduced the activation energy of the electrical conductivity into the VFT equation by establishing fitting parameters for the VFT equation via an Arrhenius equation: $\sigma_0 = \sigma_{\infty}$ and $B = E_{\sigma}/k_B$. The final version the VFT equation can therefore be expressed as follows:

$$\sigma = \sigma_{\infty} \cdot \exp(-E_{\sigma}/(k_B(T - T_0))) \quad (10)$$

The activation energies of electrical conductivities for TAPIL [P4446][BF₄] and [P4446][NTf₂] were calculated in this manner and are listed in Table 8.

3.3 Dynamic viscosity

The dynamic viscosities of the TAPILs [P4446][BF₄] and [P4446][NTf₂], as a function of temperature, are shown in Fig.4. From these values, it can be observed that the dynamic viscosity for each TAPIL decreases significantly with an increase in tem-

Table 8 Fitted parameter values of σ_0 , B , T_0 , and correlation coefficient, R , by equation (8) and activation energy, E_{σ} , for TAPILs [P4446][BF₄] and [P4446][NTf₂] by equation (10)

Parameter	[P4446][BF ₄]	[P4446][NTf ₂]
$\sigma_0/(\text{S} \cdot \text{cm}^{-1})$	11.35	1.75
B/K	2026.5	1295.4
$10^3 E_{\sigma}/\text{eV}$	174.9	111.8
T_0/K	125.5	142.6
R	0.99998	0.99997

σ_0 : the maximum electrical conductivity; B : fitting parameters;

E_{σ} : activation energy; T_0 : fitting parameter; R : correlation coefficient

Fig.3 Plots of $\ln \sigma$ vs $1/T$ of two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

perature.

VFT equation is used for fitting the temperature dependence against the dynamic viscosity for ILs. Herein, the temperature dependence of the dynamic viscosity for each of the TAPILs [P4446][BF₄] and [P4446][NTf₂] were also fitted according to the following VFT equation:

$$\eta = \eta_0 \exp(B/(T - T_0)) \quad (11)$$

where η is the dynamic viscosity; and η_0 , B , and T_0 are the fitting parameters. The best fitting parameters of η_0 , B , T_0 , and the corresponding correlation coefficient, R , are listed in Table 9. From Table 9, the obtained values of the correlation coefficient, R , are higher than 0.9999, which indicates that the VFT equation can be used for fitting the experimental dynamic viscosity.

As with the electrical conductivity, an Arrhenius equation was also used to fit the dynamic viscosity:

$$\eta = \eta_{\infty} \exp(E_{\eta}/(k_B T)) \quad (12)$$

$$\ln \eta = \ln \eta_{\infty} + (E_{\eta}/k_B)T^{-1} \quad (13)$$

where E_{η} is the activation energy for the dynamic viscosity, η_{∞} is the maximum dynamic viscosity, and k_B is the Boltzmann constant. The $1/T$ dependence of $\ln \eta$ was plotted for the TAPILs [P4446][BF₄] and [P4446][NTf₂] (see Fig.5). From Fig.5, as with the electrical conductivity shown above, the points are also not following the straight lines (The solid straight lines were drawn in order to clarify the points).

The activation energy of the dynamic viscosity was introduced

Fig.4 Plots of dynamic viscosity vs temperature of two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

Fig.5 Plots of $\ln \eta$ vs $1/T$ of two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

into the VFT equation in a similar fashion as with the electrical conductivity above, and as discussed by Vila *et al.*⁴⁶ The final version of the VFT equation can be expressed as:

$$\eta = \eta_0 \exp(E_a / (k_B(T - T_0))) \quad (14)$$

The activation energies of the dynamic viscosity for the TAPILs [P4446][BF₄] and [P4446][NTf₂] were calculated and are listed in Table 9.

3.4 Walden rule

The relationship between the molar conductivity and dynamic viscosity for TAPILs [P4446][BF₄] and [P4446][NTf₂] can be described by Walden's rule^{36,47–50}:

$$\Lambda \eta = k \quad (15)$$

where Λ is the molar conductivity, η is the dynamic viscosity, and k is a temperature dependent constant. The Walden product at 298.15 K (in [S·cm²·mol⁻¹][mP·s]) is 48 for [P4446][BF₄] and 42 for [P4446][NTf₂].

The $\lg \Lambda$ dependence on $\lg \eta^{-1}$ from 283.15 to 353.15 K is plotted in Fig.6 for the two TAPILs [P4446][BF₄] and [P4446][NTf₂]. From Fig.6, the curves are approximately straight lines, which indicates that the ILs to some extent obey Walden's rule. The slopes of the lines for the TAPILs [P4446][BF₄] and [P4446][NTf₂] are 0.931 and 0.967, respectively. These results indicate that the relationship between the conductivity and fluidity is a constant for both cases. The position of the ideal line was established by using aqueous KCl solutions at high dilution, and the lines for the two TAPILs are close to the ideal KCl line. Most of the previously reported ILs^{36,47–50} show the same tendency. The TAPILs

Fig.6 Walden plots for two TAPILs [P4446][BF₄] and [P4446][NTf₂] from 283.15 to 353.15 K

The solid straight line is the ideal line for aqueous KCl solutions at high dilution.

Fig.7 Walden plots for [P4446][NTf₂] and literature values at 298.15 K

The solid straight line is the ideal line for aqueous KCl solutions at high dilution.

[P4446][BF₄] and [P4446][NTf₂] can be called “subionic”⁵¹.

To compare Walden plots, the values for [P4446][NTf₂] and from previous literature^{40,52,53} are plotted in Fig.7.

4 Conclusions

The density, dynamic viscosity, and electrical conductivity of the air and water stable hydrophobic TAPILs [P4446][BF₄] and [P4446][NTf₂] were determined at atmospheric pressure over the temperature range from 283.15 to 353.15 K. The experimental density and electrical conductivity values for anion [NTf₂]⁻ are higher than for anion [BF₄]⁻. However, the dynamic viscosity shows the opposite trend, and the two TAPILs show very low densities. The thermal expansion coefficient, molecular volume, standard molar entropy, and lattice energy of the TAPILs were estimated by empirical equations. The two TAPILs show lower lattice energies than those of more traditional salts (e.g., CsI). The density and dynamic viscosity decrease, and the electrical conductivity increases, with an increase in temperature. The temperature dependence of the dynamic viscosity and electrical conductivity cannot be fitted by an Arrhenius equation (see Figs.3 and 5). However, the VFT equation can be used to fit the experimental values, and the TAPILs [P4446][BF₄] and [P4446][NTf₂] can be considered “subionic” according to Walden's rule.

Table 9 Fitted parameter values of η_0 , B , T_0 , and correlation coefficient, R , by equation (11) and activation energy, E_a , for TAPILs [P4446][BF₄] and [P4446][NTf₂] by equation (13)

Parameter	[P4446][BF ₄]	[P4446][NTf ₂]
η_0 /(mPa·s)	0.0085	0.0338
B /K	1922.3	1346.9
$10^3 E_a$ /eV	165.9	116.2
T_0 /K	138.2	143.8
R	0.99999	0.99999

η_0 : the maximum dynamic viscosity; B : fitting parameters; E_a : activation energy;

T_0 : fitting parameters; R : correlation coefficient

Supporting Information: The ^1H NMR spectra have been included. This information is available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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两种疏水型膦类离子液体的密度、动力粘度及电导率

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Density, Dynamic Viscosity and Electrical Conductivity of Two Hydrophobic Phosphonium Ionic Liquids

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Fig.S1 ^1H NMR of [P4446][BF₄]

Fig.S2 ^1H NMR of [P4446][NTf₂]