Surface tension and refractive index of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids

Hugo F.D. Almeida a, José A. Lopes-da-Silva b, Mara G. Freire a,*, João A.P. Coutinho a

a Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
b QOPNA Unit, Departamento de Química, Universidade de Aveiro, 3810-193, Aveiro, Portugal

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A B S T R A C T
Experimental data on the surface tension and refractive index of tetradecyltrihexylphosphonium-based ionic liquids with bromide, chloride, decanoate, methanesulfonate, dicyanamide, bis(2,4,4-trimethylpentyl)phosphinate and bis(trifluoromethylsulfonyl)imide anions are reported. The data were obtained for pure and water saturated samples at temperatures from 283 K to 353 K and at atmospheric pressure. The refractive index of the investigated ionic liquids decreases with increasing the water content in the sample. On the other hand, no clearly dependence of the surface tension with the water content up to a weight fraction of 16% was found. The prediction of the refractive index for the studied ionic liquids was also accomplished by a group contribution method and new values for the cation and diverse anions were estimated and proposed. The studied ionic liquids show lower surface tension in comparison with imidazolium-, pyridinium- or pyrrolidinium-based ionic liquids with a similar anion; also they show higher surface entropy than cyclic nitrogen-based fluids which indicates a lower surface organization. The anion dependence of the surface tension and surface entropy for the investigated ionic liquids is weaker than that for short-chain imidazolium-based ionic liquids. Their critical temperatures evaluated from Eötvös and Guggenheim equations are also lower than those of N-heterocyclic ionic fluids.

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1. Introduction

During the last decade, ionic liquids (ILs) have been largely studied and are broadly recognized as promising new solvents for industrial applications. Ionic liquids are a group of molten salts usually composed of inorganic or organic anions, and relatively large organic cations, which do not form an ordered crystal and, consequently, they remain liquid at or near room temperature [1–4]. Besides the overexplored imidazolium-based ionic liquids [5–11], new families of ionic liquids attracted increasing interest in the past few years. Among them, studies considering piperidinium-, pyridinium-, [12,13], cholinium-[14,15] and guanidinium-based [16] cations have emerged in literature. Besides these nitrogen-based ionic liquids, new classes of ionic liquids including the sulfonium- [17,18] and phosphonium-based [19,20] have also been investigated.

The Cytec Industries Inc., specialized in phosphorus specialties, produces tetralkylphosphonium ionic liquids in bulk quantities, and therefore the number of studies and industrial applications regarding phosphonium-based ionic liquids is growing progressively [4]. Phosphonium-based salts also present further advanta-
In the sequence of optimization and operation processes at the industrial level, the knowledge of the thermophysical properties of ionic liquids, such as density, viscosity, refractive index and surface tension are relevant features. In spite of a large number of studies concerning imidazolium-based ionic liquids, phosphonium-based fluids are still poorly characterized. Only a few studies report viscosities [19,29,30], densities at low and high pressures [19,31–33], surface tensions [34,35] and refractive indexes [30,36] of some phosphonium-based ionic liquids. Moreover, ionic liquids tend to be highly hygroscopic and the control of their water content at low values is not an easy task. Therefore, in this work, we present surface tension and refractive index data for seven tetradecyltrihexylphosphonium-based ionic liquids for both pure and water-saturated samples. Both properties were determined as a function of temperature, and the related surface thermodynamic functions and hypothetical critical temperatures were also estimated. The ionic liquids investigated further allow us to gather a better understanding on the anion effect upon their thermophysical properties.

2. Experimental

2.1. Chemicals

Seven tetradecyltrihexylphosphonium-based ionic liquids were studied in this work: tetradecyltrihexylphosphonium bis(trifluoromethylsulfonyl)imide \([\text{P}_{666}(14)][\text{NTf}_2]\) (mass fraction purity > 98%), tetradecyltrihexylphosphonium bromide \([\text{P}_{666}(14)][\text{Br}]\) (mass fraction purity ≈ 96% to 98%), tetradecyltrihexylphosphonium chloride \([\text{P}_{666}(14)][\text{Cl}]\) (mass fraction purity ≈ 93% to 95%), tetradecyltrihexylphosphonium decanoate \([\text{P}_{666}(14)][\text{Deca}]\) (mass fraction purity ≈ 97%), tetradecyltrihexylphosphonium methanesulfonate \([\text{P}_{666}(14)][\text{CH}_3\text{SO}_3]\) (mass fraction purity ≈ 98% to 99%), tetradecyltrihexylphosphonium dicyanimide \([\text{P}_{666}(14)][\text{N(CN)}_2]\) (mass fraction purity ≈ 97%), and tetradecyltrihexylphosphonium bis(2,4,4-trimethylpentyl)phosphinate \([\text{P}_{666}(14)][\text{Phosph}]\) (mass fraction purity ≈ 93%). All ionic liquids were kindly provided by Cytec Industries Inc. The ionic structures of the studied ionic liquids are depicted in figure 1.

Due to the low initial purity level of all samples, the ionic liquids were purified by repeatedly washing them with ultra-pure water (at least 4 times), under constant stirring for a minimum of 24 h, as previously reported by us [19]. All ionic liquids form a second liquid phase in the presence of water at room temperature. The water used was doubled distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus. After stopping the agitation, the phases were separated and the water-rich phase was removed. Thereafter, individual samples of each ionic liquid were dried at moderate temperature (≈ 232 K) and at high vacuum (≈ 10⁻⁵ Pa), under constant stirring, and for a minimum period of 48 h. After this purification procedure, the purity of all ionic liquid samples was further checked by \(^1\text{H}, \^{13}\text{C}\) and \(^{31}\text{P}\) (and \(^{19}\text{F}\) NMR for the fluorinated ionic liquid) and showed to be > 99 wt%.

The water content of each ionic liquid, after the drying step and immediately before the measurements of the thermophysical properties for pure ionic liquids, was determined by Karl Fischer titration making use of a Metrohm 831 Karl Fischer coulometer. For the water-saturated samples, the ionic liquids were left in contact with water for at least 48 h and at 298.15 K. Further details on the equilibrium procedure were previously reported [37]. The water content in the water-saturated samples was also measured by Karl Fischer titration, and the values obtained were compared with previous solubility data [19]. The saturation values of water at 298.15 K in each ionic liquid have an average relative deviation of 0.05% to those previously published [19]. The reagent employed was Hydranal–Coulomat AG from Riedel-de Haën. The water content of each “pure” ionic liquid after the drying procedure and in the water-saturated samples is presented in table 2.

2.2. Apparatus and procedure

2.2.1. Refractive index

Measurements of refractive index \((n_D)\) were performed at 589.3 nm using an automated Abbemat 500 Anton Paar refractometer, developed for measuring both liquid and solid samples. Refractive index measurements were carried out in the temperature range from (283.15 to 353.15) K for pure ionic liquids and

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FIGURE 1. Ionic structures of (a) tetradecyltrihexylphosphonium, \([\text{P}_{666}(14)]^+\); (b) bromide, Br⁻; (c) dicyanimide, \([\text{N(CN)}_2]^–\); (d) decanoate, \([\text{Deca}]^-\); (e) methanesulfonate, \([\text{CH}_3\text{SO}_3]^–\); (f) chloride, Cl⁻; (g) bis(trifluoromethylsulfonyl)imide, \([\text{NTf}_2]^–\); (h) bis(2,4,4-trimethylpentyl)phosphinate, \([\text{Phosph}]^-\).
from (298.15 to 353.15) K for water-saturated ionic liquids, at atmospheric pressure. The Abbemat 500 Anton Paar refractometer uses light to measure the refractive index, where the sample on the top of the measuring prism is irradiated from different angles by a LED. The maximum deviation in temperature is ±0.01 K and the maximum uncertainty in the refractive index measurements is ±0.00002. Previous data reported by us [38] support the applicability of the method here used to determine the refractive index of ionic liquids.

### 2.2.2. Surface tension

The surface tension of each sample was determined through the analysis of the shape of a pendant drop and measured using a DataPhysics contact angle system OCA-20. Drop volumes of (15 ± 2) μL (depending on the ionic liquid) were obtained using a Hamilton DS 500/CT syringe connected to a Teflon coated needle placed inside an aluminium air chamber able to maintain the temperature of interest within ±0.1 K. The temperature was attained by circulating water in a double jacketed aluminium cell by means of a Julabo F-25 water bath. The surface tension measurements were performed in the temperature range from 298 K to 343 K. The temperature inside the aluminium chamber in which the surface tensions were determined was measured with a Pt100 within ±0.1 K (placed at a distance of approximately 2 cm to the liquid drop). After reaching a specific temperature, the measurements were carried out after 30 min to guarantee the thermal stabilization. Silica gel was kept inside the air chamber aiming at keeping a dry environment. For the surface tensions determination at each temperature, and for each ionic liquid, at least six drops were formed and measured. For each drop, an average of 130 images was captured. The analysis of the drop shape was executed with the software modules SCA 20 where the gravitational acceleration (g = 9.8018 m s⁻²) and latitude (lat = 40°) were used according to the location of the assay. The density values required for the calculation of the surface tensions from the drop image data were taken from literature [19]. Further details on the equipment and its validity to measure surface tensions of ionic liquids were previously addressed [38,39].

### 3. Results and discussion

#### 3.1. Refractive index

The refractive index data for pure tetracycltriexylphosphonium- and water-saturated tetracycltriexylphosphonium-based ionic liquids at several temperatures are presented in tables 2 and 3, respectively.

For a common temperature, the refractive index values for the pure tetracycltriexylphosphonium-based ionic liquids decrease in the follow anionic sequence: Br⁻ > [N(CN)₂]⁻ > Cl⁻ > [CH₃SO₃]⁻ > [PF₆]⁻ > [NTf₂]⁻. The results also indicate that the refractive index of the studied ionic liquids slightly decreases with an increase in temperature. For ionic liquids having imidazolium-based cations, it was previously demonstrated that the refractive index increases with the following anionic trend: Cl⁻ > [CH₃SO₃]⁻ > [CF₃SO₃]⁻ > [NTf₂]⁻ > [BF₄]⁻ > [PF₆]⁻ [40]. Therefore, it seems that the refractive index depends slightly on the anionic volume. Indeed, several equations have been proposed to determine the molar refraction or molar polarizability making use of density data [36]. As stated by Deetlefs et al. [41], an implication of some of these approaches is that the refractive index of a substance is higher when its molecules are more tightly packed, i.e., when the compound is denser. Taking into account this hypothesis, the refractive indices obtained in this work were correlated with the ionic liquids molar volumes (determined from density literature data [19]). The results obtained are depicted in figure 2 where a dependence of the refractive index with the ionic liquid molar volume is observed. The scattering of the data on this figure may be related with the observation of Tariq et al. [36] that showed an inverse dependency between the densities and refractive indices for the series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. In fact, care must be taken when generalizing some relations commonly employed to isotropic fluids since the nanostructure of ionic liquids [42,43] may hinder their application. This may be particularly relevant for ionic liquids with long alkyl chains [36].

The prediction of the refractive index for the ionic liquids studied was also accomplished making use of the group contribution approach $A_i$ and $B_i$ parameters to calculate the molar refractions or molar polarizabilities.
method proposed by Gardas and Coutinho [40], according to the following equation,

\[ n_D = A_{nD} - B_{nD} T, \]  

where

\[ A_{nD} = \sum_{i=1}^{k} n_i a_{nD i}, \]  

\[ B_{nD} = \sum_{i=1}^{k} n_i b_{nD i}, \]  

where \( n_i \) is the number of group of type \( i \), and \( k \) is the total number of different groups in the molecule.

The estimated parameters \( a_{nD i} \) and \( b_{nD i} \) for the studied pure ionic liquids are given in table 4, and the comparison between the experimental data and the group contribution method is depicted in figure 3. New values for \( a_{nD i} \) and \( b_{nD i} \) for the ions \([P666(14)][NTf_2]\), \([P666(14)][Deca]\), \([P666(14)][Phosph]\), \([P666(14)][N(CN)2]\) and \([P666(14)][Cl]\) were estimated with the data collected in this work. The average absolute relative deviation between the experimental and the fitting data are 0.02% for \([P666(14)][NTf_2]\), 0.01% for \([P666(14)][Deca]\), 0.01% for \([P666(14)][Phosph]\), 0.01% for \([P666(14)][N(CN)2]\), 0.01% for \([P666(14)][Cl]\), 0.01% for \([P666(14)][CH3SO3]\).

For the water-saturated phosphonium-based salts the refractive index decreases in the following rank: \([N(CN)2]^- > Br^- > Cl^- > [Phosph]^- > [CH3SO3]^- > [Deca]^- > [NTf2]^-\). Figure 4 depicts the dependence of the variation of the refractive index of the several ionic liquids, presented as the difference between the water-saturated refractive index and pure refractive index \((\Delta n_D)\) with the water content difference between the water-saturated and the "neat" sample \((\Delta H_2O)\) wt%, at 298.15 K.
For all samples, the refractive index of the water-saturated tetradecyltrihexylphosphonium-based ionic liquids is lower than that of the pure ionic liquids. In general, the refractive index decreases with increasing water content on the ionic liquid, albeit a slight increase is observed for the two more complex ionic liquids: \([\text{P666(14)}][\text{Deca}]\) and \([\text{P666(14)}][\text{Phosph}]\). In fact, the ionic liquid with the lowest water content, \([\text{P666(14)}][\text{NTf2}]\), only shows a deviation on the refractive index in the order of \(-4 \times 10^{-3}\). Due to its fluorinated anion, \([\text{P666(14)}][\text{NTf2}]\) dissolves very low amounts of water [19]. Our results agree with previous ones on the refractive index of aqueous solutions of ionic liquids [44,45] where the refractive index decreases with increasing water content.

### 3.2. Surface tension

The surface tensions of pure and water-saturated tetradecyltrihexylphosphonium-based ionic liquids are presented in tables 5 and 6, respectively. For a better analysis on the temperature influence, and on the quasi-linear dependence of surface tension with temperature, the results for pure ionic liquids are calculated from the respective experimental density data at 298.15 K [19]. This dependence on the molar volume was previously observed by us with imidazolium-based fluids [39,48] and it is shown here to extend to phosphonium-based ionic liquids.

For a common temperature, the surface tensions of the water-saturated tetradecyltrihexylphosphonium-based ionic liquids decrease in the same sequence observed for the pure ionic liquids: \([\text{P666(14)}][\text{N(CN)}2] > [\text{P666(14)}][\text{CH3SO3}] \approx [\text{P666(14)}][\text{Cl}] > [\text{P666(14)}][\text{Br}] > [\text{P666(14)}][\text{Deca}] > [\text{P666(14)}][\text{Phosph}]\). Therefore, independently of the water content (up to the saturation level in phosphonium-based salts) no variations in the general trend are observed. Despite this one we must be aware that the presence of water greatly influences the surface tension of the sample, as previously observed for imidazolium-based ionic liquids [7]. A decrease in the surface tension was observed for low water contents, whereas for higher amounts of water, the surface tensions reach values close to those of “pure” ionic liquids [7]. Aiming at evaluating the effect of water in the surface tension of phosphonium-based salts, the variation on the surface tension, defined as the difference between the surface tension of the water-saturated samples and the pure ionic liquids, as a function of the water content is depicted in figure 5. In fact, there is a decrease in the surface tension of \([\text{P666(14)}][\text{NTf2}]\), the ionic liquid with the lower amount of water, and an increase in the surface tension for the remaining ionic liquids with higher water contents. As previously established by us [7] at low water concentrations the water migrates to the near-surface region of the ionic liquid establishing

### Table 5

<table>
<thead>
<tr>
<th>([\text{P666(14)}][\text{NTf2}])</th>
<th>([\text{P666(14)}][\text{Deca}])</th>
<th>([\text{P666(14)}][\text{Phosph}])</th>
<th>([\text{P666(14)}][\text{N(CN)}2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>((\gamma \pm 2\sigma/\gamma)) (mN m(^{-1}))</td>
<td>T/K</td>
<td>((\gamma \pm 2\sigma/\gamma)) (mN m(^{-1}))</td>
</tr>
<tr>
<td>298.2</td>
<td>30.1 \pm 0.1</td>
<td>298.0</td>
<td>29.0 \pm 0.2</td>
</tr>
<tr>
<td>307.9</td>
<td>29.5 \pm 0.1</td>
<td>307.9</td>
<td>28.5 \pm 0.2</td>
</tr>
<tr>
<td>317.9</td>
<td>28.7 \pm 0.2</td>
<td>318.0</td>
<td>27.8 \pm 0.2</td>
</tr>
<tr>
<td>327.9</td>
<td>28.1 \pm 0.1</td>
<td>328.5</td>
<td>27.2 \pm 0.2</td>
</tr>
<tr>
<td>337.8</td>
<td>27.5 \pm 0.2</td>
<td>338.0</td>
<td>26.6 \pm 0.2</td>
</tr>
<tr>
<td>343.2</td>
<td>27.3 \pm 0.2</td>
<td>343.0</td>
<td>26.2 \pm 0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>([\text{P666(14)}][\text{Br}])</th>
<th>([\text{P666(14)}][\text{Cl}])</th>
<th>([\text{P666(14)}][\text{CH3SO3}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>((\gamma \pm 2\sigma/\gamma)) (mN m(^{-1}))</td>
<td>T/K</td>
</tr>
<tr>
<td>298.2</td>
<td>30.9 \pm 0.2</td>
<td>298.6</td>
</tr>
<tr>
<td>308.5</td>
<td>30.2 \pm 0.2</td>
<td>308.0</td>
</tr>
<tr>
<td>318.0</td>
<td>29.6 \pm 0.1</td>
<td>318.0</td>
</tr>
<tr>
<td>338.6</td>
<td>28.7 \pm 0.2</td>
<td>338.1</td>
</tr>
<tr>
<td>343.4</td>
<td>27.9 \pm 0.2</td>
<td>343.3</td>
</tr>
</tbody>
</table>

\(a\) Expanded uncertainty at the 0.95 confidence level, \(2\sigma/\gamma\), evaluated from the standard deviation and applying a coverage factor \(k = 2\).
hydrogen-bonding interactions with the anion while leading to a decrease on the cohesive energy of the ionic liquid. The addition of extra water leads to the appearance of water molecules not hydrogen-bonded to the ionic liquid and to the development of water clusters, and thus to an increase in the surface tension values.

In spite of the significance of surface tension data in a wide range of applications in pure and applied sciences, the data available are scarce when taking into account the large number of possible ionic liquids that can be synthesized. The data for phosphonium-based fluids are indeed scarce [49]. Between the ionic liquids studied, surface tension data for \([\text{P666}(14)]\text{NTf}_2\) [34,35], \([\text{P666}(14)]\text{Deca}\) [34], \([\text{P666}(14)]\text{Phosph}\) [34,50], and \([\text{P666}(14)]\text{N(CN)2}\) [34,50] were found in literature. Whereas Carrera et al. [50] reported surface tensions only at room temperature, Carvalho et al. [35] and Kilaru et al. [34] evaluated the influence of temperature in the surface tensions of \([\text{P666}(14)]\text{NTf}_2\), \([\text{P666}(14)]\text{Cl}\) and \([\text{P666}(14)]\text{N(CN)2}\). The relative deviations between our data and those from literature [34,35,50] are observed among our data and literature data. For instance, positive relative deviations are observed for \([\text{P666}(14)]\text{Cl}\) [34] and \([\text{P666}(14)]\text{N(CN)2}\) [50] (1.20% and 5.19%, respectively), whereas negative relative deviations are encountered for \([\text{P666}(14)]\text{NTf}_2\) [34,35], \([\text{P666}(14)]\text{Cl}\) [34] and \([\text{P666}(14)]\text{N(CN)2}\) [34]. The purification technique used in this work for the ionic liquid samples is similar to that reported by Carvalho et al. [35]. The data reported by the authors were measured using a different technique (Du Noüy ring); yet, low relative deviations are observed between our results and the published data [35]. On the other hand, large deviations are observed between our results and the data provided by Kilaru et al. [34]. Large average relative deviations are particularly observed for \([\text{P666}(14)]\text{Cl}\), \([\text{P666}(14)]\text{N(CN)2}\) and \([\text{P666}(14)]\text{NTf}_2\) (−8.12%, −7.19% and −8.29%, respectively). Therefore, these large relative deviations are a main consequence of the samples purity: traces of tetradecene isomers, HCl, and \([\text{PR}3\text{H}]\text{Cl}\). Large deviations among our data and literature data [35] and the published data [34].

The surface thermodynamic properties, namely surface entropy and surface enthalpy, can be estimated based on the quasi-linear dependence of the surface tension with temperature (shown in figure 5). The surface entropy, \(S^\circ\), can be calculated according to \([51,52]\).

\[
S^\circ = -\frac{d\gamma}{dT}
\]

(4)

while the surface enthalpy, \(H^\circ\), according to \([51,52]\).

\[
H^\circ = \gamma - T\left(\frac{d\gamma}{dT}\right)
\]

(5)

where \(\gamma\) stands for the surface tension, and \(T\) for the temperature.
The values of the thermodynamic functions for the pure and water-saturated tetradecyltriethylphosphonium-based ionic liquids, along with their standard deviations [53], are presented in Table 7.

In agreement with the results previously reported for different cation-based ionic liquids [5,7,35,38,39], this class of fluids reveals surprisingly low surface entropies when compared with molecular organic compounds. These values reflect a high surface organization, as well as an inherent highly structured liquid phase in ionic liquids. However, phosphonium-based ionic liquids present slightly higher surface entropies than their imidazolium-based counterparts [7,39], which indicate a lower surface organization. In previous works we have addressed the effect of the alkyl chain length and the effect of the cation core and anion nature [5,35,38,39] on the surface entropy of pure and water-saturated ionic liquids in the temperature range between 283 K and 353 K.

The critical temperature of fluids, $T_c$, is an important property used in corresponding states relations concerning equilibrium and transport properties [54]. However, the determination of the critical temperatures of ionic liquids is impossible since they decompose long before reaching those high temperature values. Rebelo et al. [55] proposed the use of the Eötvös [56] and Guggenheim [57] equations to estimate the hypothetical critical temperatures of ionic liquids. Although the authors acknowledge that this method “allows only for rough estimates of the critical temperatures” and should therefore be used with caution, recent results from molecular simulations by Rai and Maggin [16,58] suggest that the critical temperatures estimated by these simple methods are in good agreement with those obtained by molecular simulation. The critical temperature values determined from the surface tension data obtained in this work are reported in Table 7. The phosphonium-based ionic liquids present lower critical temperatures than imidazolium-, pyridinium, or pyrrolidinium-based ionic liquids with a common anion [35,39].

4. Conclusion

New experimental data were reported for the refractive index and surface tension of seven ionic liquids with the tetradecyltriethylphosphonium cation combined with the anions bis(trifluoromethylsulfonyl)imide, bromide, chloride, decanoate, methanesulfonate, dicyanamide and bis(2,4,4-trimethylpentyl)phosphinate. The experimental data were measured for both pure and water-saturated ionic liquids in the temperature range between 283 K and 353 K.

The surface tension and the refractive index decrease with the temperature increase and are generally dependent on the anion which composes a given ionic liquid. A slight dependence with the ionic liquids molar volume was observed for both properties. In general, water-saturated ionic liquids present lower refractive index and higher surface tension values when compared to the pure samples.

The surface thermodynamic functions were also investigated and reveal that phosphonium-based ionic liquids present higher surface entropies than their imidazolium-based counterparts, indicating thus a lower surface organization of these long alkyl chain fluids. In addition, the effect of the ionic liquid anion in phosphonium-based salts seems to be less relevant in their surface organization. The hypothetical critical temperatures were also estimated and tend to be lower than those offered by cyclic-nitrogen-based fluids.

Acknowledgments


<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>$(S^\text{a} \pm \sigma^\text{a}) \times 10^{-2} \text{(J m}^{-2}\text{K}^{-1})$</th>
<th>$(H^\text{a} \pm \sigma^\text{a}) \times 10^{-2} \text{(J m}^{-2})$</th>
<th>$(T_c)_{\text{exp}}/K$</th>
<th>$(T_c)_{\text{calcd}}/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P666(14)][NTf2]</td>
<td>6.6 ± 0.2</td>
<td>7.02 ± 0.08</td>
<td>4.98 ± 0.05</td>
<td>5.09 ± 0.03</td>
</tr>
<tr>
<td>[P666(14)][Deca]</td>
<td>6.2 ± 0.1</td>
<td>7.7 ± 0.1</td>
<td>4.75 ± 0.04</td>
<td>5.23 ± 0.04</td>
</tr>
<tr>
<td>[P666(14)][Phosph]</td>
<td>7.05 ± 0.09</td>
<td>6.6 ± 0.3</td>
<td>4.93 ± 0.03</td>
<td>4.82 ± 0.09</td>
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<tr>
<td>[P666(14)][N(CN)2]</td>
<td>6.4 ± 0.1</td>
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<td>5.14 ± 0.04</td>
<td>5.20 ± 0.05</td>
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<td>6.9 ± 0.1</td>
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<td>[P666(14)][CI]</td>
<td>7.21 ± 0.2</td>
<td>7.6 ± 0.2</td>
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<td>5.36 ± 0.05</td>
</tr>
<tr>
<td>[P666(14)][CH3SO4]</td>
<td>6.8 ± 0.1</td>
<td>7.0 ± 0.1</td>
<td>5.13 ± 0.04</td>
<td>5.22 ± 0.04</td>
</tr>
</tbody>
</table>

$^a$ Standard deviation.