Polyoxometalates in Imidazolim-based Ionic Liquids: Acceptor Number and Polarity estimated from their Voltammetric Behaviour

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The selection of an appropriate solvent is essential for achieving high yields and selectivity in chemical reactions. The chemical and physical parameters of organic solvents have been classified into several groups, and solvents can be compared with each other with respect to these properties. The acceptor number (A_N), donor number (D_N) and polarity (E_T^N) have been widely accepted and used for theoretically and quantitatively evaluating the properties of organic solvents. In a similar manner, the A_N, D_N and E_T^N of room temperature ionic liquids (RTILs) have been estimated from spectral changes in solvatochromic compounds. In this paper, the A_N and E_T^N of eight types of imidazolium-based RTILs were estimated from the relationship between the A_N and E_T^N values and the first redox potential obtained from the voltammograms of polyoxometalates (POMs) in various organic solvents. The obtained parameters were compared with those estimated by spectrophotometric methods reported previously by several groups. This new method for estimating the A_N and E_T^N of RTILs using the voltammetric behaviour of POMs with low charge density and high symmetry could provide the other path to obtain more reliable A_N and E_T^N of RTILs.

Keywords: Polyoxometalates, ionic liquids, acceptor number, polarity, cyclic voltammetry

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**Introduction**

A variety of ionic liquids have been prepared, characterized and applied in various fields since reports on so-called “room temperature ionic liquids (RTILs)” suggested that these materials are liquids even below 100°C.\(^1\) RTILs have two roles, as solvents and solutes (salts), and they have been used as solvents (instead of water and organic solvents) for organic syntheses and as salts for electrochemistry.\(^2\)\(^,\)\(^3\) RTILs, which are nonvolatile and reusable, exhibit fascinating chemical properties. The use of RTILs instead of classic organic solvents has allowed higher yields and selectivity in many organic syntheses.\(^4\)-\(^9\) Furthermore, RTILs with high conductivity have been used as liquid salts for next-generation batteries.\(^10\),\(^11\) The biological applications of RTILs in drug synthesis and drug delivery have been extensively investigated due to their bioactivity.\(^12\) In addition, RTILs have been applied in electrochemical biosensors to detect a variety of biomolecules, such as dopamine, uric acid, ascorbic acid and nitrogen oxide, and the addition of other materials, such as graphene and carbon nanotubes, has been used to enhance the detection sensitivity.\(^13\),\(^14\) RTILs have also been used as media for gas sensing due to their nonvolatility and conductivity.\(^15\)-\(^20\) Understanding the fundamental properties of RTILs could clarify the mechanism of their function as solvents and as ions. Many researchers have tried to distinguish organic solvents based on their physical and chemical properties and have provided various useful parameters for these analyses, such as the dielectric constant, acceptor number (A\(_N\)), donor number (D\(_N\)), and polarity (E\(_T^N\)).\(^21\) Such parameters are quite important for selecting the best solvent for a specific chemical reaction and investigating the reaction mechanism in detail. Since ionic liquids have two faces as the solvent and the solute, as described above, accurate A\(_N\) and D\(_N\) values could not be obtained using the traditional methods used for organic solvents. Such solvent properties of RTILs have been investigated by using spectrophotometry with various solvatochromic probes to estimate A\(_{NS}\), D\(_{NS}\), E\(_{TN}\)\(_S\), and other parameters.

Polyoxometalates (POMs) are a class of metal-oxide clusters that consist of tungsten and molybdenum as addenda atoms, sulfur and phosphorus as heteroatoms, and oxygen. The electrochemical properties of POMs have been extensively investigated in aqueous solutions, organic solvents and mixed solvents since they can undergo reversible multielectron transfer processes without structural changes.\(^22\)-\(^24\) The anion charge of Keggin- and Wells-Dawson-type POMs (Figure 1) with frameworks composed of only molybdate or tungstate is related to their redox potential under neutral conditions. The first redox waves appeared at more positive potentials as the anionic charge of the POMs decreased, and a linear relationship between the redox potential and the anion charge or bond length between the tungsten in the framework and the oxygen attached to heteroatoms was obtained.\(^25\)-\(^27\) In addition, the first redox potentials observed in organic solvents were related to the A\(_N\) and E\(_T^N\) of organic solvents, which indicates that the redox potentials of POMs can be used as a probe for the electrochemical determination of A\(_N\) and E\(_T^N\) of various solvents.\(^27\),\(^28\) Tetraphenylarsonium tetrphenylborate was selected as a standard compound for the determination of the transfer activity coefficients of individual cations and anions from water to organic solvents.\(^21\) This compound consists of large, similarly sized monocations and monoanions with high symmetry,
resulting in no specific interactions between the organic solvents and the ions due to the low and uniform surface charge density of the tetraphenylarsonium cations and the tetraphenylborate anions. Similarly, POMs have high symmetry and low surface charge density, indicating that they would be good standard compounds for evaluating the chemical properties of organic solvents in a manner similar to tetraphenylarsonium tetraphenylborate.

Several dyes have been used as solvatochromic probes for determining the $A_{NS}$ and $D_{NS}$ and $E_{TN}$ of ionic liquids with spectrophotometric methods. Since such parameters are relative but not absolute values, alternative methods that are unrelated to spectrophotometry should be developed to validate the parameters of the RTILs and provide higher accuracy and reliability.

In the present study, the voltammetric behaviours of Keggin-type POMs, $[SVW_{11}O_{40}]^{3-}$ and $[PVW_{11}O_{40}]^{4-}$, and Wells-Dawson-type POMs, $[S_2W_{18}O_{62}]^{4+}$ and $[P_2W_{18}O_{62}]^{6-}$, were investigated in organic solvents such as acetonitrile, acetone, dimethyl formamide, dimethyl sulfoxide, nitromethane, and propylene carbonate to obtain the relationship between their redox potentials and the organic parameters. The electrochemical redox behaviour of POMs in RTILs was investigated, and the solvent parameters of the RTILs were determined from the observed redox potentials of the RTILs and the obtained relationship in organic solvents.

**Experimental**

$[(n-C_4H_9)N]_3[SVW_{11}O_{40}](SVW_{11}), [(n-C_4H_9)N]_4[PVW_{11}O_{40}](PVW_{11}), [(n-C_3H_7)N]_4[S_2W_{18}O_{62}](S_2W_{18})$ and $[(n-C_4H_9)N]_6[P_2W_{18}O_{62}](P_2W_{18})$ were synthesized according to synthetic procedures reported in the literature. Tetrabutylammonium hexafluorophosphate, $[n-Bu_4N][PF_6]$, was purchased from Tokyo Chemical Industry (98.0%) and recrystallized three times from ethanol for use as a supporting electrolyte. Acetone (ACE) (HPLC-MS grade; 99.7%), dimethyl formamide (DMF), acetonitrile (ACN) (LC-MS grade; 99.8%) and dimethyl sulfoxide (DMSO) (99.95%) were purchased from WAKO Chemicals. Propan-2-ol (≥98.0%) was acquired from Sigma-Aldrich, Japan. Propylene carbonate (PC) (99.7%) and six types of ionic liquids, namely, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM[BF$_4$]), hexafluorophosphate (BMIM[PF$_6$]), trifluoromethanesulfonate (BMIM[OTf]) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM[BF$_4$]), ethyl sulfate (EMIM[EtSO$_4$]), and trifluoromethanesulfonate (EMIM[OTf]), were acquired from Sigma-Aldrich, Japan. Two types of ionic liquids, 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonil)imide, BMIM[NTf$_2$] and EMIM[NTf$_2$], respectively, were purchased from Tokyo Chemical Industry, Japan (Figure 1S), and nitromethane (NM) (≥98.0%) was acquired from Nacalai Tesque, Inc. Molecular sieves (Type 3A, 1/16) were used to remove water from the ionic liquids. The POMs were dissolved in ionic liquids using an ultrasonic bath or heating at 70-80°C because of the high viscosity of the ionic liquids. Cyclic voltammograms were measured with a CV-50 W instrument (BAS, Japan). Glassy carbon electrodes (BAS, Japan) with surface areas of 0.0079 cm$^2$ and 0.071 cm$^2$ were used as the working electrode, and a platinum wire was used as the counter electrode for the RTILs and organic solvents. The reference electrode was a silver wire, which was set in a sample glass tube containing organic
solvents in the presence of 0.1 M $n$-Bu$_4$NPF$_6$ with porous glass attached to the solution or platinum wire in ionic liquids. The measured potential versus Ag or Pt was converted to the Fe/Fe$^+$ scale using data derived from voltammograms for oxidation of ferrocene in organic solvents and RTILs. Prior to each measurement, the working electrode was polished manually with a 0.1 μm diamond slurry and washed with distilled water and acetone.

**Results and Discussion**

**Cyclic voltammograms of polyoxometalates in organic solvents**

Cyclic voltammograms of 0.5 mM POM solutions were measured in ACE, DMF, PC, ACN, DMSO and NM in the presence of 0.1 M $n$-Bu$_4$NPF$_6$ (Figure 2). The $n$-Bu$_4$N$^+$ cation slightly influences the voltammetric behaviour of POMs, while protons as well as small cations as Li$^+$ drastically do. On the other hand, lower concentrations of electrolyte give rise to higher resistance. In this study, the concentrations of $n$-Bu$_4$NPF$_6$ were set to 0.1 M. Although PVW$_{11}$ was not fully dissolved in ACE, this did not influence the redox potential. The first two reduction waves for all POMs are described in Figure 2. Each of the midpoint potentials, $E_m=(E_{pc}+E_{pa})/2$, where $E_{pc}$ is the cathodic (reduction) potential and $E_{pa}$ is the anodic (oxidation) potential, is listed in Table 1. The peak potential separations ($\Delta E$ values) between the reduction potential and oxidation potential peaks ranged from 50 to 70 mV for each redox process, indicating that all the redox processes are reversible. All the redox processes are diffusion-controlled because each of the observed current magnitudes is proportional to the square root of the scan rates (20-500 mV/s). The first electron transfer process is ascribed to the redox of the vanadium component (V/IV) of SVW$_{11}$ and PVW$_{11}$, while all the other electron transfer processes are ascribed to redox processes of the tungsten component (VI/V).

Afterwards, the following electrochemical reactions occur reversibly:

For XVW$_{11}$ (X=S, P)

1$^{\text{st}}$ step: XV$^{\text{V}}$W$^{\text{VI}}$_{11} + e$^-$ ⇄ XV$^{\text{IV}}$W$^{\text{V}}$_{11}

2$^{\text{nd}}$ step: XV$^{\text{IV}}$W$^{\text{VI}}$_{11} + e$^-$ ⇄ XV$^{\text{IV}}$W$^{\text{V}}$W$^{\text{VI}}$_{10}

For X$_2$W$_{18}$ (X=S, P)

1$^{\text{st}}$ step: X$_2$W$^{\text{VI}}$_{18} + e$^-$ ⇄ X$_2$W$^{\text{V}}$W$^{\text{VI}}$_{17}

2$^{\text{nd}}$ step: X$_2$W$^{\text{V}}$W$^{\text{VI}}$_{17} + e$^-$ ⇄ X$_2$W$^{\text{V}}$W$^{\text{V}}$W$^{\text{VI}}$_{16}

The redox potentials of the parent (no metal-substituted) Keggin- and Wells-Dawson-type POMs observed under neutral conditions, where no protons are coupled, are related to the total anionic charge of the POMs and the bond length of W-$\mu_4$O. In addition, these potentials are also related to the A$_N$S of the organic solvents. Recently, the first redox potentials of mono vanadium-substituted Keggin-type POMs, XVM$_{11}$ (X=S, P, As; M=Mo, W) and Wells-Dawson type [S$_2$VW$_{17}$O$_{62}$]$^{5-}$ were found to be related to A$_N$ and E$_T$N. In this study, the mean first redox potentials ($E_{m,\text{org}}^{1\text{st}}$) of all the POMs (calculated from the cyclic voltammograms and measured five times) were plotted against the A$_N$S and E$_T$N's of the organic solvents to provide a linear relationship (Table 1, Figure 3). The following equations were estimated:

\[ E_{m}^{1\text{st}} = aA_N + b \]  \( (1) \)
\[ E_{m}^{1st} = cE_N + d \]  

where the constants a, b, c and d are shown in Table 2. These equations could provide the \( A_N \) and \( E_T^N \) values if the first redox potentials were obtained in any solvent (Table 1).

**Estimation of the acceptor number and polarity of ionic liquids**

The voltammetric behaviours of four POMs were investigated in eight types of ionic liquids. In the case of SVW\(_{11}\) and PVW\(_{11}\), the solution changed to pale blue without electrochemical reduction because the POMs were partially reduced due to their high reactivity in ionic liquids\(^{43, 44}\). The real reactions that occur during dissolution have not yet been elucidated because they do not affect the electrochemical redox potentials. Although small anodic currents are present, even at the starting potential, the first midpoint potentials were determined from a couple of reduction/oxidation waves by the same method as organic solvents (Figure 4, Table 3). The peak potential separations (\( \Delta E \) values) between the reduction potential and oxidation potential peaks ranged from 75 to 120 mV for each redox process, indicating that all the redox processes are quasi-reversible. The diffusion coefficients of the reduced (\( D_{\text{red}} \)) and oxidized (\( D_{\text{ox}} \)) species are quite different in RTILs, unlike organic solvents\(^{45}\). This could affect the difference between the midpoint potentials and the formal potentials\(^{46}\). However, the charge density of POMs would not change drastically by one-electron reduction because of the large size of POMs, indicating that the diffusion coefficients of the reduced and oxidized forms of POMs would be similar. Even if \( D_{\text{red}}/D_{\text{ox}} \) is not equal to the reported values, \( E_m \) changes in the experimental error, which is less problematic for determining \( A_N \) and \( E_T^N \). In this paper, the \( E_m \) was determined by the same method as organic solvents. The linear relationship between the observed current magnitude at each reduction step and the square root of the scan rates indicated that all the redox processes are diffusion-controlled, and the diffusion coefficients (\( D_{\text{POM,IL}} \)) are given by the Randles-Sevcik equation\(^{46}\):

\[
i_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} n^1 A^{1/2} D^{1/2} C^{1/2} v^{1/2}
\]

Due to the high viscosity of ionic liquids, the \( D_{\text{POM,IL}} \) values are very low, ranging from \( 10^{-8} \) to \( 10^{-9} \) (Table 1S)\(^{47}\). The diffusion coefficients of SVW\(_{11}\) in EMIM[C\(_2\)H\(_5\)OSO\(_3\)] and BMIM[PF\(_6\)], PVW\(_{11}\) in BMIM[NTf\(_2\)], and S\(_2\)W\(_{18}\) in EMIM[C\(_2\)H\(_5\)OSO\(_3\)], EMIM[NTf\(_2\)] and BMIM[NTf\(_2\)] were not calculated because SVW\(_{11}\), PVW\(_{11}\) and S\(_2\)W\(_{18}\) were partially reduced or not fully dissolved in those ionic liquids. \( E_{pc} \) and \( E_{pa} \) were checked to calculate \( E_{m,IL}^{1st} \) from the obtained cyclic voltammograms in ionic liquids. Although the solubilities of SVW\(_{11}\) in EMIM[EtOSO\(_3\)] and BMIM[PF\(_6\)] and PVW\(_{11}\) in BMIM[NTf\(_2\)] were low, the concentrations of the POMs in the RTILs had less influence on \( E_{pc} \) and \( E_{pa} \) as they did in organic solvents. The cyclic voltammograms of the POMs in RTILs were measured at least five times to verify \( E_{pc} \) and \( E_{pa} \). The \( A_N \) and \( E_T^N \) values were estimated using eqs. (1) and (2) (Tables 4 and 5), respectively. The errors calculated by error propagation of the slopes and intercepts of linear regression analyses were not small. However, \( A_N \) and \( E_T^N \) are not absolute values, such as physical constants and the concentrations of compounds, and would contain errors, although such errors have
not been reported. Different values of various chemical parameters as well as $A_N$ and $E_T^N$ have been reported depending on the measurement techniques and chemical probes used. $^{48}$ The calculated errors are thought to be in an acceptable range. Even when different POMs were used, similar $A_N$ and $E_T^N$ were estimated, although both values, which were calculated from the first redox potentials of P$_2$W$_{18}$, were higher in all the ionic liquids. Even if different POMs were used and different $E_{m,S}$ were obtained, similar $A_N$ and $E_T^N$ values were estimated. Several groups have reported the $A_{NS}$ of RTILs determined from spectroscopic methods such as Raman and NMR. Similar $A_{NS}$ were obtained even when different methods were used. The values were similar to those calculated from the $E_{m,IL,1st}$ of P$_2$W$_{18}$ and were larger than those obtained by using SVW$_{11}$ and S$_2$W$_{18}$. Imidazolium RTILs with different carbon chains and the same anion exhibit smaller $A_{NS}$ as the carbon chain becomes longer. $^{33}$ The same trend was also observed for EMIM and BMIM with [OTf], [BF$_4$], and [NTf$_2$] in this study. Solvatochromic dyes, which are not highly symmetric molecules and are partially charged (either positive or negative), could specifically interact with the anion and cation of the RTILs, resulting in some errors in the solvent parameters, such as in $A_N$ and $D_N$. Indeed, detailed interactions between RTILs and solvatochromic dyes as well as POMs should be investigated to evaluate the more precise solvent parameters of RTILs in the future. The $A_N$ and $D_N$ of the RTILs were estimated by considering the interactions with both the anionic and cationic parts, which are completely different from those obtained by the other groups. $^{34}$

Similarly, several different $E_T^N$s were obtained, even in the same RTILs. $^{29, 31, 36}$ The $E_T^N$s calculated from the $E_{m,IL,1st}$ of SVW$_{11}$ and S$_2$W$_{18}$ were those from the $E_{m,IL,1st}$ of P$_2$W$_{18}$, which are similar to most reported $E_T^N$s. $A_N$ and $E_T^N$ values have been widely accepted for quantitatively evaluating solvent properties. Molecules with a lower charge density and higher symmetry, such as tetrphenylarsonium tetraphenylborate, are thought to be good probes for investigating interactions with solvent molecules. $^{21}$ We have also investigated solvent parameters by using [SM$_{12}$O$_{40}$]$^2^-$ ($M=Mo, W$), which has a smaller total anionic charge. However, these compounds were less soluble in the RTILs, and cyclic voltammograms could not be obtained.

In the present study, a new method for estimating the $A_N$ and $E_T^N$ of RTILs by using the redox potentials of POMs was developed. POMs with low charge density and high symmetry should exhibit weaker specific interactions with RTILs, which should be good probes for exploring the chemical parameters, $A_{NS}$ and $E_T^N$s, of RTILs. The $A_{NS}$ and $E_T^N$s of other RTILs could be obtained by changing the countercation of the POM to increase the solubility of the RTILs.

**Conclusions**

In the present study, the $A_N$ and $E_T^N$ values of RTILs were electrochemically estimated by using the relationship between the first redox potentials of POMs ([XVW$_{11}$O$_{40}$]$^n^-$, ($X=S(n=3), P(n=4)$) and [X$_2$W$_{18}$O$_{42}$]$^{n^+}$ ($X=S(n=4), P(n=6)$)) and the $A_{NS}$ and $E_T^N$s in conventional organic solvents. Cyclic voltammograms of XVW$_{11}$ and X$_2$W$_{18}$ ($X=P, S$) were measured in organic solvents such as acetone, dimethyl formamide, propylene carbonate, acetonitrile, dimethyl sulfoxide, and nitromethane at least five times to obtain $E_{pe}$ and $E_{pa}$ from the first one-electron transfer process with high precision. The
midpoint potentials, $E_{m,org}^{1st}$, calculated from $E_{pc}$ and $E_{pa}$ for all POMs were linearly related to $A_N$ and $E_T^N$, and a simple equation was determined to express the relationship between $E_{m,org}$ and $A_N$ or $E_T^N$. In a similar manner, the cyclic voltammograms of XVW$_{11}$ and X$_2$W$_{18}$ (X=P, S) were also measured in eight different RTILs to obtain $E_{pc}$ and $E_{pa}$ from the first one-electron transfer process and to calculate $E_{m,ILs}^{1st}$, which gave the $A_{NS}$ and $E_T^N$s of the RTILs from the equations of the relationship between $E_{m,org}$ and $A_N$ or $E_T^N$. Most of the obtained $A_{NS}$ and $E_T^N$s are comparable with those reported by several researchers (Tables 4 and 5). In the present study, although the $A_{NS}$ and $E_T^N$ of only eight ionic liquids were estimated due to the solubility of the POMs, the use of different countercations changed the solubility of the POMs, so the $A_{NS}$ and $E_T^N$s of all the RTILs could be electrochemically determined using this method. POMs are good probes for estimating the $A_N$ and $E_T^N$ values of ionic liquids since they interact less with ionic liquids due to their low total anionic charge, charge density, and high symmetry. It is of great importance and interest to compare electrochemically determined chemical parameters of RTILs with those from conventional spectrophotometric measurements to find more appropriate values that can express chemical phenomena and reactions in RTILs.

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### Table 1

Mean midpoint potentials (\(E_{\text{m1}}^{\text{s}}/\text{mV vs Fc/Fc}^{+}\)) of the first redox process corresponding to \(V^{V/IV}\) in SVW\textsubscript{11} and PVW\textsubscript{11} and to \(W^{VI/V}\) in S\textsubscript{2}W\textsubscript{18} and P\textsubscript{2}W\textsubscript{18}.

| POMs     | Acetone | DMF   | PC    | Acetonitrile | DMSO  | Nitromethane |
|----------|---------|-------|-------|--------------|-------|--------------|
| SVW\textsubscript{11} | 50±10   | 40±1  | 260±1 | 150±2        | 180±2 | 200±2        |
| PVW\textsubscript{11} | -520±2  | -500±1| -180±1| -310±2       | -260±5| -220±2       |
| S\textsubscript{2}W\textsubscript{18} | -460±5  | -370±1| -150±1| -260±2       | -210±2| -220±1       |
| P\textsubscript{2}W\textsubscript{18} | -1170±2 | -1170±3| -820±3| -940±2       | -900±2| -850±2       |

\(A_N\) = acceptor number; \(E_T^{N}\) = polarity. See ref. [21].

### Table 2

Slope (a, c), intercept (b, d) and correlation coefficient (r) of equations (1, 2) expressing the relationship between the midpoint potentials of the POMs observed in organic solvents and the acceptor number or polarity.

| POMs     | a   | b            | c            | d            | r  |
|----------|-----|--------------|--------------|--------------|----|
| SVW\textsubscript{11} | 23±10 | -2.5±1.7\times10^2 | 1.5±0.3\times10^3 | -4.9±1.3\times10^2 | 0.93 |
| PVW\textsubscript{11} | 44±13 | -1.1±0.2\times10^3 | 2.6±0.3\times10^3 | -1.4±0.1\times10^3 | 0.97 |
| S\textsubscript{2}W\textsubscript{18} | 36±9 | -9.0±1.7\times10^2 | 2.0±0.4\times10^3 | -1.1±0.2\times10^3 | 0.93 |
| P\textsubscript{2}W\textsubscript{18} | 47±14 | -1.8±0.3\times10^3 | 2.8±0.3\times10^3 | -2.2±0.1\times10^3 | 0.97 |
Table 3 Mean midpoint potentials ($E_{\text{m}}^{1\text{st}}/\text{mV vs Fc/Fc}^+$) corresponding to $V^{1/1}$ for SVW$_{11}$ and PVW$_{11}$ and $W^{1/1}$ for S$_2$W$_{18}$ and P$_2$W$_{18}$ in various ionic liquids.

| POMs | EMIM[OTf] | EMIM[BF$_4$] | EMIM[EtOS O$_3$] | EMIM[NTE$_2$] | BMIM[OTf] | BMIM[BF$_4$] | BMIM[Pf$_6$] | BMIM[NTE$_2$] |
|------|------------|--------------|------------------|--------------|------------|--------------|--------------|--------------|
| SVW$_{11}$ | 240±1       | 550±1        | 405±3            | 355±13       | 180±2      | 335±11       | 415±3        | 60±1         |
| PVW$_{11}$ | -40±5       | 200±4        | 40±1             | 60±4         | -90±1      | -245±4       | 70±1         | -180±2       |
| S$_2$W$_{18}$ | -100±2      | 155±4        | -                | -            | -190±3     | -130±1       | 25±3         | -            |
| P$_2$W$_{18}$ | -370±2      | -350±3       | -305±4           | -390±6       | -450±5     | -450±4       | -450±1       | -390±3       |

Table 4 Acceptor numbers of various ionic liquids estimated from the first midpoint potentials of SVW$_{11}$, PVW$_{11}$, S$_2$W$_{18}$ and P$_2$W$_{18}$.

| POMs | EMIM[OTf] | EMIM[BF$_4$] | EMIM[EtOS O$_3$] | EMIM[NTE$_2$] | BMIM[OTf] | BMIM[BF$_4$] | BMIM[Pf$_6$] | BMIM[NTE$_2$] |
|------|------------|--------------|------------------|--------------|------------|--------------|--------------|--------------|
| SVW$_{11}$ | 22±9        | 35±15        | 29±13            | 27±12        | 19±8       | 26±11        | 30±13        | 11±5         |
| PVW$_{11}$ | 24±8        | 30±9         | 26±8             | 27±8         | 23±7       | 20±6         | 27±8         | 21±6         |
| S$_2$W$_{18}$ | 23±6        | 30±8         | -                | -            | 20±5       | 22±6         | 26±8         | -            |
| P$_2$W$_{18}$ | 31±9        | 32±9         | 28±8             | 30±9         | 29±9       | 29±9         | 30±9         | -            |

reported | 37.1 | 33.5 | 25.0 | 27.4 | 28.46 | 29.26 | 29.66 | 30.05 |

(a) see ref. [33]; (b) see ref. [32]; (c) see ref. [30]; (d) see ref. [34]

Table 5 Polarities of various ionic liquids estimated from the first midpoint potentials of SVW$_{11}$, PVW$_{11}$, S$_2$W$_{18}$ and P$_2$W$_{18}$.

| POMs | EMIM[OTf] | EMIM[BF$_4$] | EMIM[EtOS O$_3$] | EMIM[NTE$_2$] | BMIM[OTf] | BMIM[BF$_4$] | BMIM[Pf$_6$] | BMIM[NTE$_2$] |
|------|------------|--------------|------------------|--------------|------------|--------------|--------------|--------------|
| SVW$_{11}$ | 0.5±0.1    | 0.7±0.1      | 0.6±0.1          | 0.6±0.1      | 0.45±0.09  | 0.6±0.1      | 0.34±0.07    | 0.6±0.1      |
| PVW$_{11}$ | 0.56±0.07  | 0.65±0.08    | 0.59±0.08        | 0.60±0.08    | 0.54±0.07  | 0.48±0.06    | 0.50±0.07    | 0.60±0.08    |
| S$_2$W$_{18}$ | 0.5±0.1    | 0.6±0.1      | -                | -            | 0.47±0.09  | 0.50±0.1     | 0.6±0.1      | -            |
| P$_2$W$_{18}$ | 0.65±0.07  | 0.65±0.07    | 0.60±0.07        | 0.64±0.07    | 0.62±0.07  | 0.62±0.07    | 0.64±0.07    | -            |

reported | 0.71 | 0.685 | 0.667 | 0.664 | 0.669 | 0.654 | 0.519 | 0.522 | 0.656 |

(a) see ref. [36]; (b) see ref. [29]; (c) see ref. [31]
Figure 1 Polyhedral presentation of (a) Keggin- and (b) Wells-Dawson-type POMs
Figure 2 Cyclic voltammograms of 0.5 mM (a) SVW$_{11}$, (b) PVW$_{11}$, (c) S$_2$W$_{18}$, and (d) P$_2$W$_{18}$ in acetone (ACE), dimethyl formamide (DMF), propylene carbonate (PC), acetonitrile (ACN), dimethyl sulfoxide (DMSO) and nitromethane (NM) containing 0.1 M [n-Bu$_4$N][PF$_6$]. Scan rate: 100 mVs$^{-1}$
Figure 3 Relationships between the (A) acceptor number ($A_N$) and (B) polarity ($E_T^N$) of organic solvents and $E_{m,org}^{1st}$ of (a) SVW$_{11}$, (b) S$_2$W$_{18}$, (c) PVW$_{11}$ and (d) P$_2$W$_{18}$. 
Figure 4 Cyclic voltammograms of 0.5 mM (A) SVW\textsubscript{11}, (B) PVW\textsubscript{11}, (C) S\textsubscript{2}W\textsubscript{18} and (D) P\textsubscript{2}W\textsubscript{18} in (a) BMIM[BF\textsubscript{4}], (b) BMIM[OTf], (c) EMIM[PFI], (d) BMIM[NTf\textsubscript{2}], (e) EMIM[BF\textsubscript{4}], (f) EMIM[OTf], (g) EMIM[EtOSO\textsubscript{3}] and (h) EMIM[NTf\textsubscript{2}].