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Solvation structure and thermodynamics for Pr(III), Nd(III) and Dy(III) complexes in ionic liquids evaluated by Raman spectroscopy and DFT calculation

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ABSTRACT

The coordination states of trivalent praseodymium, neodymium, and dysprosium complexes in the ionic liquid, triethyl-*n*-pentylphosphonium bis(trifluoromethyl-sulfonyl) amide ([P_{2225}][TFSA]) were investigated by Raman spectroscopy. The effect of the concentration of rare earth ions on the Raman spectra was investigated, ranging from 0.23 to 0.45 mol kg^{-1} of Pr(III), Nd(III), and Dy(III) in [P_{2225}][TFSA]. Based on a conventional analysis, the solvation numbers, *n*, of Pr(III), Nd(III), and Dy(III) in [P_{2225}][TFSA] were determined to be 4.99, 5.01, and 5.00 at 298 K and 5.04, 5.06, and 5.07 at 373 K, respectively.

Thermodynamic properties such as $\Delta_{iso}G$, $\Delta_{iso}H$, and $\Delta_{iso}S$ for the isomerism of $[TFSA]^-$ from *trans*- to *cis*-coordinated isomer in the bulk and the first solvation sphere of the central RE^{3+} (RE = Pr, Nd, and Dy) cation in [P_{2225}][TFSA] were evaluated from the temperature dependence of the Raman bands, measured at temperatures ranging from 298 to 398 K. Regarding the bulk properties, $\Delta_{iso}G$(bulk), $\Delta_{iso}H$(bulk), and $T\Delta_{iso}S$(bulk) at 298 K were found to be −1.06, 6.86, and 7.92 kJ mol^{-1}, respectively. The *trans*-$[TFSA]^-$ was a dominant contributor to the enthalpy, as shown by the positive value of $\Delta_{iso}H$(bulk). The value of $T\Delta_{iso}S$(bulk) was slightly larger than that of $\Delta_{iso}H$(bulk), and *cis*-$[TFSA]^-$ was, therefore, entropy-controlled in [P_{2225}][TFSA]. In contrast, in the first solvation sphere of the RE^{3+} cation, $\Delta_{iso}H$(RE) became remarkably negative, suggesting that *cis*-$[TFSA]^-$ isomers were stabilized by enthalpic contributions. Furthermore, $\Delta_{iso}H$(RE) contributed to the remarkable decrease in $\Delta_{iso}G$(RE), and this result clearly indicates that *cis*-$[TFSA]^-$ conformers bound to RE^{3+} cations are the preferred coordination state of $[RE^{(III)}(cis\text{-}TFSA)_5]^{2-}$ in [P_{2225}][TFSA].

Moreover, optimized geometries and binding energies of $[Pr^{(III)}(cis\text{-}TFSA)_5]^{2-}$, $[Nd^{(III)}(cis\text{-}TFSA)_5]^{2-}$, and $[Dy^{(III)}(cis\text{-}TFSA)_5]^{2-}$ clusters were also investigated by DFT calculations using the ADF package. The bonding energy, ΔE_b, was calculated as $\Delta E_b = E_{tot}(cluster) - E_{tot}(RE^{3+}) - nE_{tot}([TFSA]^-)$, and ΔE_b ($[Pr^{(III)}(cis\text{-}TFSA)_5]^{2-}$), $\Delta E_b([Nd^{(III)}(cis\text{-}TFSA)_5]^{2-})$, and $\Delta E_b([Dy^{(III)}(cis\text{-}TFSA)_5]^{2-})$ were calculated to be −4238.6 ± 6.8, −4362.3 ± 8.2, and −4284.2 ± 7.4 kJ mol^{-1}, respectively. This series of structural results allows us to conclude that $[Dy^{(III)}(cis\text{-}TFSA)_5]^{2-}$ clusters are more stable state than the $[Pr^{(III)}(cis\text{-}TFSA)_5]^{2-}$ clusters in [P_{2225}][TFSA]. Furthermore, the average atomic charges and the bond distances of these clusters were consistent with the thermodynamic properties.

1. Introduction

Rare earth (RE) elements are indispensable in high-tech industries due to their physicochemical properties, having a range of uses, for example, as abrasives, catalysts, fluorescent substances, and permanent magnets [1–4]. In particular, Nd-Fe-B permanent magnets are finding increasing applications in a broad range of fields and are used for a variety of industrial products, such as voice coil motors, magnetic resonance imaging, and hybrid-type electric vehicles [5–7]. However, almost one-fourth of the alloy material produced is wasted as useless scraps formed during the manufacturing processes. Consequently, the development of a recovery process of RE elements from the Nd-Fe-B magnet scraps would be valuable. We have previously demonstrated an

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electrodeposition method for Nd [8–12] and Dy [13,14] metals using room-temperature ionic liquids (RTILs) with the bis(trifluoromethyl-sulfonyl)amide, $[TFSA]^-$, anion. RTILs have several distinctive properties such as low vapor pressures, incombustibility, high ionic conductivity, and a wide electrochemical window [15,16]. In particular, phosphonium ILs containing the $[TFSA]^-$ anion are appropriate for the electrodeposition of RE metals because of their low viscosities, high thermal stabilities, and wide electrochemical windows in comparison with imidazolium-based ILs [17].

In general, in ILs, metal ions are solvated by several molecular dipoles to form metal ion solvated clusters [18]. The electrodeposition process is affected significantly by the solvation structure of the metal ions in the ILs. There have been some reports concerning the solvation structures of various metal ions, Li [19–23], Mn [24,25], Fe [26], Co [24,26], Ni [24,26], Zn [24], Nd [10,27], Eu [28], and Dy [29], in TFSA-based ILs as determined by Raman spectroscopy. However, there have been few reports concerning the analysis of the solvation structures at elevated temperatures or thermodynamic analyses concerning the isomerism of the $[TFSA]^-$ anion, which can isomerize between *trans* and *cis* isomers in the bulk and in the first solvation sphere of the RE ions dissolved in ILs. Therefore, we investigated the solvation number at elevated temperature and the isomerization characteristics of the $[TFSA]^-$ ligands of Pr(III), Nd(III), and Dy(III) complexes by studying the temperature dependence of the Raman bands. In addition, theoretical DFT calculations were carried out using the Amsterdam Density Functional (ADF) program (version 2014.01) [30–34], and we have used these results to discuss the optimum geometries of these complexes in depth. The ADF package enables us to perform full-electron calculations for all elements including the heavy RE elements.

Therefore, by combining an experimental approach and computational analysis, we have gained a thorough understanding of the coordination states of RE complexes in ILs. In this work, the solvation number and the $[TFSA]^-$ isomer analysis of Pr(III), Nd(III), and Dy(III) complexes in TFSA-based ILs were investigated by band intensity analysis and thermodynamic analysis using Raman spectroscopy. Moreover, the optimum geometries and the bonding energies of these complexes were also examined using the ADF package to understand the stability of their coordination states.

2. Experimental

2.1. Preparation

The IL triethyl-*n*-pentylphosphonium bis(trifluoromethyl-sulfonyl)amide, $[P_{2225}][TFSA]$, used in this study was synthesized by the metathesis reaction of $[P_{2225}]Br$ (Nippon Chemical Industrial Co., Ltd., >99.5%) and Li[TFSA] (Kanto Chemical Co., Inc., 99.7%), as described previously [35]. The absence of a bromide anion in IL was confirmed by using $AgNO_3$ after repeated washing of the IL with distilled water. The obtained $[P_{2225}][TFSA]$ was dried under high vacuum < −0.1 MPa at 393 K for more than 48 h. $Pr(TFSA)_3$, $Nd(TFSA)_3$, and $Dy(TFSA)_3$ salts were synthesized by a neutralization reaction between Pr_2O_3 (Wako Chemical Industries Ltd, 99.9%), Nd_2O_3 (Wako Pure Chemical Industries Ltd, 99.9%), Dy_2O_3 (Kanto Chemical Co., Inc., 99.95%), and 1,1,1-trifluoro-*N*-[(trifluoromethyl) sulfonyl] methanesulfonamide (HTFSA, Kanto Chemical Co., Inc., >99.8%) in aqueous solution. The unreacted acid and water components in the resulting products were removed by evaporation at 393 K. The obtained $Pr(TFSA)_3$, $Nd(TFSA)_3$, and $Dy(TFSA)_3$ salts were dried in vacuo < −0.1 MPa at 393 K for 24 h.

2.2. Raman spectroscopy

First, four solutions containing Pr(III), Nd(III), and Dy(III) were prepared for the analysis of solvation number. Appropriate amounts of $Pr(TFSA)_3$, $Nd(TFSA)_3$, and $Dy(TFSA)_3$ salts were dissolved in $[P_{2225}][TFSA]$ at concentrations of 0.23, 0.30, 0.38, and 0.45 mol kg^{-1}, respectively. Raman spectra (NRS-4100, JUSCO Corp.) were measured at 298 and 373 K using a 532-nm laser for Nd and 785-nm laser for Pr and Dy. The appropriate gratings for the collection of the Raman spectra were 1800 mm^{-1} for Nd, and 1200 mm^{-1} for Pr and Dy. These conditions were adopted to prevent fluorescence of the RE ions, and the selection of these gratings is based on the results of our recent investigations [26,27].

Regarding the analysis of isomerism thermodynamics, the molar fractions of RE(III) in the sample solutions, x_{RE}, were 0.000, 0.033, 0.055, and 0.075. Raman spectra were measured at various temperatures, i.e., 298, 323, 348, 373, and 398 K. All Raman spectra were measured by accumulating 512 individual measurements to improve the signal-to-noise ratio. The overlapping Raman bands were deconvoluted into individual components using a pseudo-Voigt function.

2.3. Calculation methods

DFT calculations of the cation and anion components of the $[P_{2225}][TFSA]$ ILs were carried out using the Gaussian09 program [36]. The DFT calculations on models of the $[P_{2225}]^+$ and $[TFSA]^-$ ions were performed at the B3LYP/6-31G(d,p) [37–41] and B3LYP/6-31+G(d) level, respectively. Subsequently, frequency analysis was carried out on the optimized geometries. The hybrid functional B3LYP, which includes a mixture of Hartree-Fock exchange and DFT exchange-correlation, is Becke's three-parameter hybrid method (B3) [42] with non-local correlation provided by the Lee, Yang, and Parr (LYP) functional [43]. The 6-31G basis set with diffuse and polarization functions was used for all atoms.

In contrast, geometry optimizations of $[Pr^{(III)}(cis\text{-}TFSA)_5]^{2-}$, $[Nd^{(III)}(cis\text{-}TFSA)_5]^{2-}$, and $[Dy^{(III)}(cis\text{-}TFSA)_5]^{2-}$ were performed using the Amsterdam Density Functional (ADF) program [34] using BP (Becke88-Perdew86 functional [44–47]) and TZP basis set for Pr, Nd, and Dy, and the BP/DZP basis sets for light elements. In contrast to Gaussian, ADF uses Slater-type orbitals (STO), which describe atomic orbitals more exactly than the Gaussian orbitals (GTO) used in Gaussian09. Moreover, all-electron and frozen-core basis sets are available for all elements including lanthanides and actinides on the basis of the Zeroth-Order Regular Approximation (ZORA) method [48–50]. The frozen-core approximation can be used to reduce the computation time for systems with heavy nuclei.

3. Results and discussion

3.1. Analysis of the solvation number

The concentration dependences of the deconvoluted Raman spectra in the frequency range 720–780 cm^{-1} for concentrations of Pr(III), Nd(III), and Dy(III) samples ranging from 0.23 to 0.45 mol kg^{-1} in $[P_{2225}][TFSA]$ are shown in Fig. 1(a)–(c), respectively. Raman spectra in this range were separated into two components, one at approximately 740 cm^{-1} and the other at 751 cm^{-1}. The Raman bands can be attributed to the combination of stretching, $\nu_s(SNS)$, and bending vibrations, $\delta_s(CF_3)$, of the $[TFSA]^-$ anion [51,52]. These two bands at 740 and 751 cm^{-1} arise from the free $[TFSA]^-$ anion and the $[TFSA]^-$ anion bound to the RE metal ion, respectively. As can be seen from Fig. 1, a new band at 751 cm^{-1} is present as a shoulder of the band at 740 cm^{-1}. This new band intensified with increasing concentration of RE(III) in the IL. The