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Synthesis of Aromatic and Aliphatic N-Heterocyclic Salts and Their Application as Organic Electrolyte Supporters in Electrochemical Capacitor

Young-Ji Kim¹, Jae-Yeong Choi², Soo-Yeoun Kim^{1,*} and Seong-Ho Choi^{1,2,*}

- ¹ Department of Cosmetic Science, Hannam University, Daejeon 34054, Korea; a01089615001@gmail.com
- ² Department of Chemistry, Hannam University, Daejeon 34054, Korea; feelcjy@hnu.kr
- * Correspondence: cozy0570@gmail.com (S.-Y.K.); shchoi@hnu.kr (S.-H.C.)

Abstract: Aromatic and aliphatic N-heterocyclic chemical salts were synthesized by counteranion-exchange reactions after substitution reactions in order to apply them as organic electrolyte supporters in an electrochemical capacitor (super capacitor). The aromatic N-heterocyclic salts were N-methylpyridinium tetrafluoroborate ([MPy]⁺[BF₄]⁻), N-methylpyridinium hexafluorophosphate ([MPy]⁺[PF₆]⁻), 1,3-dibuthylimidazolium tetrafluoroborate ([DI]⁺[BF₄]⁻), 1,3dibuthylimidazolium hexafluorophosphate ([DI]+[PF₆]⁻), 1-buthyl-4-methyl-1,2,4-triazolium tetrafluoroborate ([BMTA]⁺[BF₄]⁻), and 1-buthyl-4-methyl-1,2,4-triazolium hexafluorophosphate ([BMTA]⁺[PF₆]⁻). The aliphatic N-heterocyclic salts were N,N-dimethylpiperilidium tetrafluoroborate ([DMP]⁺[BF₄]⁻), N,N-dimethylpiperilidium hexafluorophosphate ([DMPy]⁺[PF₆]⁻), N,N-dimethylpyrrolidium tetrafluoroborate ([DMPy]⁺[BF₄]⁻) and N,N-dimethylpyrrolidium hexafluorophosphate ([DMPy]⁺[PF₆]⁻), 1-ethyltriethamine tetrafluoroborate ([E-TEDA]⁺[BF₄]⁻), and 1-ethyltriethamine hexafluorophosphate ([E-TEDA]⁺[PF₆]⁻), respectively. We confirmed the successful synthesis of the aromatic and aliphatic N-heterocyclic chemical salts by ¹H-NMR, FT-IR, and GC/MS analysis before conducting the counter-anion-exchange reactions. Then, we determined the electrochemical potential of vanadium acetylacetonate (V(acac)₃) under acetonitrile in the presence of the N-heterocyclic chemical salts as energy-storage chemicals. By cyclic voltammetry, the maximum voltages with the N-heterocyclic chemical salts in acetonitrile reached 2.2 V under a fixed current value. Charge-discharge experiments were performed in the electrochemical capacitor with an anion-exchange membrane using a non-aqueous electrolyte prepared with a synthesized N-heterocyclic salt in acetonitrile.

Keywords: vanadium electrochemical capacitor; N-heterocyclic aromatic salts; N-heterocyclic aliphatic salts; vanadium acetylacetonate; energy-storage chemicals; counter-anion-exchange reaction

1. Introduction

Electrochemical capacitors (supercapacitors) are good energy-storage systems. A typical electrochemical capacitor consists of two electrodes, an ion-permeable membrane, and an electrolyte packaged in a sealed container [1,2]. The electrodes are mainly composed of carbon materials with electrical conductivity and energy-storage capacity [3,4]. The separator is mainly made of an insulating polymer (e.g., polyethylene, polypropylene, poly[tetrafluoroethylene], etc.) used as a porous, thin film [5,6]. The electrolyte is composed of a material with high ionic conductivity along with electrochemical and thermal stability. Commonly used electrolytes are aqueous solutions such as sulfuric acid (H_2SO_4) [7], potassium hydroxide (KOH) [8], organic electrolytes based on propylene carbonate and acetonitrile [9–11], and ionic liquids consisting of cations, such as imidazolium, pyridinium, and quaternary ammonium, and anions, such as halogen, tetrafluoroborate, and hexafluorophosphate [12,13]. Most of these aqueous electrochemical capacitor systems cause undesirable ion cross-over because of the membrane's permeability, which leads



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to power and energy loss. Another problem of the aqueous electrochemical capacitor system is the low cell potential because of the aqueous electrolyte solutions [14]. On the other hand, non-aqueous systems exhibit wide potential windows and a wide temperature range compared with aqueous systems because of the physical and chemical properties of the non-aqueous electrolyte solution [15]. Despite the advantages of a non-aqueous electrolyte solution in the electrochemical capacitor, there have been few studies of this setup because of the difficulties in synthesizing the organic electrolyte, the low solubility of vanadium salts as energy-storage materials, and the physical problem of the membrane for ion exchange during the charge-discharge process under a non-aqueous electrochemical capacitor.

To solve the above-mentioned problems, this study synthesized the N-heterocyclic chemical salts $[MPy]^+[BF_4]^-$, $[MPy]^+[PF_6]^-$, $[DI]^+[BF_4]^-$, $[DI]^+[PF_6]^-$, $[BMTA]^+[BF_4]^-$, $[DMP]^+[BF_4]^-$, $[DMP]^+[BF_4]^-$, $[DMPy]^+[BF_4]^-$, $[DMPy]^+[PF_6]^-$, $[E-TEDA]^+[BF_4]^-$, and $[E-TEDA]^+[PF_6]^-$ through counter-anion-exchange reactions after the SN2 reaction. Proton nuclear magnetic resonance (¹H-NMR), Fourier transform infrared (FT-IR), and gas chromatography with mass spectrometry (GC/MS) were used to confirm the synthesized products during the reaction. The main aim of this study was to investigate the solubility of vanadium acetylacetonate (V(acac)_3) in organic solvents with synthesized chemical salts and its electric properties, such as electrochemical potential and capacity of synthesized aromatic and aliphatic N-heterocyclic chemical salts.

2. Experimental Procedure

2.1. Materials

Pyridine, 1-butylimidazole, triazole, 1-methylpiperidine, 1-methylpyrrolidine, triethyldiamine (TEDA), methyl bromide, butyl bromide, butyl iodide, methyl iodide, ethyl bromide, sodium tetrafluoroborate, sodium hexafluorophosphate, acetonitrile (99.8%), propylene carbonate, 1,4-dioxide, and V(acac)₃ were purchased from Sigma-Aldrich (St. Louis, MO, USA). The commercial membrane for anion exchange was obtained from Innomeditech Inc. (Neosepta-AFN, Seoul, Korea). The whole chemicals and solvents were used without any purification.

2.2. Synthesis of the Aromatic and Aliphatic N-Heterocyclic Salts

The schematic syntheses of the aromatic and aliphatic N-heterocyclic salts by the counter-ion-exchange reactions after the SN2 reactions were shown in Figures 1 and 2. In detail, first, $[MPy]^+[I]^-$ was synthesized by the SN2 reaction between Py (10.0 mmol) and methyl iodide (10.0 mmol) under acetonitrile at room temperature for 24 h. After the reaction, we added ether to remove unreacted reactants and then obtained the $[MPy]^+[I]^-$. This process was performed three times to obtain pure $[MPy]^+[I]^-$. After obtaining pure $[MPy]^+[I]^-$, we dried it in a vacuum oven at 60 °C overnight (about 12 h). The other aromatic and aliphatic N-heterocyclic chemical salts were obtained by the same synthesis method with the different chemicals listed above.



Figure 1. Schematic synthesis of the N-heterocyclic aromatic salts by SN2 reaction.



Figure 2. Schematic synthesis of the N-heterocyclic aliphatic salts by SN2 reaction.

The [MPy]⁺[BF₄]⁻ and [MPy]⁺[PF₆]⁻ were obtained by counterion-exchange reactions using NaBF₄ and NaPF₆ under acetonitrile at room temperature for three days while being vigorous stirred. The other aromatic and aliphatic N-heterocyclic chemical salts with [BF4] and $[PF_6]$ counterions were synthesized in a similar synthesis method as described above and as shown in Figures 1 and 2.

2.3. Characterizations

1H-NMR (Inova 600, Varian, Australia), FT-IR (FTS-175C, Bio-Rad Laboratories Inc., Hercules, CA, USA), and GC/MS (Clarus 600 series, PerkinElmer, Waltham, MA, USA) were used to confirm the aromatic and aliphatic N-heterocyclic chemical salts during the synthesis. The results we obtained by ¹H-NMR, FT-IR, and GC/MS for each synthesized chemical salt are as follows: $[MPy]^+[I]^{-:1}H$ -NMR $\delta = 4,77$ (s), 8.08 (t), 8.48 (t), and 9.36 (d) ppm; $[DI]^+[Br]^{-:1}H$ -NMR $\delta = 0,90$ (t), 1.19 (m), 1.78 (m), 4.18 (t), 7.89 (d), 7.89 (d), and 9.51 (s) ppm. MS:M⁺ = 124; $[BMTA]^+[BF4]^{-:1}H$ -NMR $\delta = 0,90$ (t), 1.18 (m), 1.75 (m), 4.18 (t), 7.91 (d), and 9.45 (s) ppm; $[DMPy]^+[I]^{-:1}H$ NMR $\delta = 2,07$ (t), 3.17 (s), and 3.42 (t) ppm. IR: = 2945 (C-H), 1460 (C-N) cm⁻¹; $[DMP]^+[I]^{-:1}H$ -NMR $\delta = 1,06$ (m), 2.08 (m), 4.98 (s), and 4.98 (t) ppm. IR: = 2945 (C-H), 1460 (C-N) cm⁻¹, $[E-TEDA]^+[Br]^{-:1}H$ -NMR $\delta = 1,5$ (t), 2.98 (t), 3.21 (t), and 3.21 (t) ppm. MS: M⁺ = 141. As a result, it was confirmed that the aromatic and aliphatic N-heterocyclic chemical salts were synthesized well.

Cyclic voltammograms (CVs) for V(acac)₃ in acetonitrile were obtained using a Versa-STAT 3 Potentiostat Galvanostat (AMETEK, Inc., Berwyn, PA, USA) by three electrodes: an Ag/AgNO₃ (0.1 M tetrabutylammonium hexafluorophosphate acetonitrile) reference electrode, a platinum wire counter electrode, and composite-coated glassy carbon (GC; diameter, 3.0 mm) working electrode.

The charge-discharge cycles were performed using a single-cell flow device with two half-cells separated by the membrane for anion exchange (Neosepta-AFN). The measurements of the charge-discharge cycles were performed by an automatic battery cycler (WBCS3000, WonATech, Seoul, Korea) under acetonitrile and 0.01 M V(acac)₃ with 0.1 M synthesized N-heterocyclic chemical salts.

In this system, the negative electrolytes, such as $[PF_6]^-$ and $[BF_4]^-$, were transported through the anion exchange membrane during the charge-discharge process. However, the positive electrolytes and vanadium cations (V(acac)₃⁺) prohibited the permeability of the membrane due to the Donnan effect [16], as shown in Figure 3.



Figure 3. Chemical structure of the commercial anion-exchange membrane (Neosepta[®] AFN) and images of the single cell for electrochemical capacitor performance.

3. Results and Discussion

Some synthesized N-heterocyclic chemical salts (i.e., $[DI]^+[Br]^-$, $[DMP]^+[Br]^-$, and $[BMTA]^+[I]^-$ of the aromatic selection, and $[MPy]^+[I]^-$, $[DMPy]^+[I]^-$, and $[E-TEDA]^+[Br]^-$ of the aliphatic selection) could not be used as electrolyte supporters under the chargedischarge process in a non-aqueous electrochemical capacitor because the $[Br]^-$ and $[I]^-$, as counter anions, could behave as Lewis bases and react with the vanadium cation. Furthermore, a self-redox reaction of the $[Br]^-$ and $[I]^-$ could occur under the chargedischarge process as shown in reactions (1) and (2); therefore, this study did not use them as electrolyte supporters in the organic electrochemical capacitor.

$$3Br^{-} \stackrel{\pm 2e}{\leftrightarrow} Br_2 + Br^{-} \rightleftharpoons Br_3^{-}$$
 (1)

$$3I^{-} \stackrel{\pm 2e}{\leftrightarrow} I_{2} + I^{-} \rightleftharpoons I_{3}^{-}$$
⁽²⁾

We evaluated the oxidation (O) and reduction (R) peaks of $V(acac)_3$ under acetonitrile with the aromatic and aliphatic N-heterocyclic salts to determine the electrochemical potential of $V(acac)_3$.

The CVs of the V(acac)₃ under acetonitrile with aromatic N-heterocyclic salts $([MPy]^+[BF_4]^-, [MPy]^+[PF_6]^-, [DI]^+[PF_6]^-, [DI]^+[PF_6]^-, [BMTA]^+[BF_4]^-, and [BMTA]^+[PF_6]^-)$ were obtained on the glassy carbon working electrode with a scan rate of 100 mV/s, as shown in Figure 4. The redox couple's voltage ranges were observed to be -2.5 to 1.0 V, depending on the electrolytes (i.e., salts), and the current peaks were observed according to reactions (3) and (4) below:

$$R_1/O_1: V(III)(acac)_3 + e^- \rightleftharpoons V(II)(acac)_3^-$$
(3)

$$R_2/O_2: V(III)(acac)_3 \rightleftharpoons V(IV)(acac)_3^+ + e^-$$
(4)



Figure 4. Cyclic voltammograms (CV) of 0.01 M V(acac)₃ under acetonitrile with 0.1 M aromatic N-heterocyclic salts on a glassy carbon working electrode with a scan rate of 100 mV/s.

The electrochemical potential of active species $V(acac)_3$ was determined to be about 2.2 V for each aromatic N-heterocyclic salt electrolyte (i.e., $[MPy]^+[BF4]^-$, $[MPy]^+[PF6]^-$, $[BMTA]^+[BF4]^-$, $[BMTA]^+[PF6]^-$, $[DI]^+[BF4]^-$, and $[DI]^+[PF6]^-$). This result means that the energy storage capacity of the V(acac)₃ can achieve a maximum of 2.2 V for each supporting electrolyte. However, the CVs of the V(acac)₃ under acetonitrile with aliphatic N-heterocyclic salts (i.e., $[DMP]^+[BF4]^-$, $[DMP]^+[PF6]^-$, $[DMPy]^+[BF4]^-$, $[DMPy]^+[PF6]^-$, $[E-TEDA]^+[BF4]^-$, and $[E-TEDA]^+[PF6]^-$) did not obtain because the aliphatic N-heterocyclic salts could degrade during the redox process.

Figures 5 and 6 show the electrochemical capacitor performance for 0.01 M V(acac)₃ under acetonitrile electrolytes in the presence of 0.1 M aromatic and aliphatic N-heterocyclic salts. The experimental condition used was as follows: voltage = 2.5 V, $I_c = 0.1$ mA, and $I_d = -0.1$ mA, and was applied using a commercial Neosepta-AFN membrane in a flow cell (see Figure 3). Regarding charge, the counter anions were transferred through the anion-exchange membrane from the reduction cell to the oxidation cell, while the electrolyte cations and the charged V(acac)₃⁺ could not be transferred through the anion-exchange membrane because of the Donnan exclusion effect [16]. The voltage distance of the charge-discharge of the V(acac)₃ under acetonitrile electrolytes with the aromatic and aliphatic



N-heterocyclic salts as supporters reached 2.2 V. Unfortunately, the charge-discharge cycles could not be measured more than 20 times because the commercial anion-exchange membrane was dissolved due to the usage of electrolytes.

Figure 5. Electrochemical capacitor performance of 0.1M V(acac)₃ in acetonitrile in the presence of 0.1 M N-heterocyclic aromatic salts (Working condition: set voltage = 2.5 V, $I_c = 0.1$ mA, and $I_d = -0.1$ mA, Neosepta[®] AFN).



Figure 6. Electrochemical capacitor performance in acetonitrile with 0.01M V(acac)₃ and 0.1 M electrolyte salts (Working condition: set voltage = 2.5 V, $I_c = 0.1 \text{ mA}$, and $I_d = -0.1 \text{ mA}$, Neosepta[®] AFN).

According to previous studies, the solubility of energy-storage chemicals increases with the use of a mixture of solvents [17]. In these cases, a phenomenon known as preferential solvation occurs, and it can be used to explain how interactions between different types of solvents affect solute-solvent interactions. In addition, Möller et al. were successful in using a solvent-mixture approach for other storage systems, such as lithium-ion batteries [18]. Therefore, for energy-storage systems such as electrochemical capacitors, this approach can provide better active species. The investigation of the solubility of V(acac)₃ was performed with different binaries as well as an increase in energy density due to the improved solubility of the ternary mixtures in the presence of aromatic and aliphatic N-heterocyclic salts (Table 1). According to the results of the solubility of the vanadium complex, the higher solubility was observed when using mixed solvents with high donor numbers or higher polarizability, such as dimethyl sulfoxide (DMSO). A ternary mixture solution with DMSO and 1,4-Di to AN or PC has a solubility almost as high as that of $V(acac)_3$, as shown in Table 1. It is known from previous reports that DMSO interacts preferentially with dissolved species because of its high donor and acceptor numbers [19]. We examined charge-discharge performance using the electrolyte mixtures; however, we could not obtain charge-discharge profiles because the assembled commercial membrane in the test cell dissolved in the electrolyte mixtures. For commercialization, these results indicate the need for an advanced anion-exchange membrane that is insoluble in electrolyte mixtures.

Table 1. Solubility of the V(acac)₃ in polar organic solution in the presence of N-heterocyclic aromatic salts ^(a).

No.	ACN	PC	DMSO	1,4-Di	[MPy] ⁺ [I] ⁻	[MPy] ⁺ [BF ₄] ⁻	[MPy] ⁺ [PF ₆] ⁻
1	100	-	-	-	0.88 M	0.88 M	0.88 M
2	94.1	-	5.90	-	0.85 M	0.85 M	0.85 M
3	76.2	-	4.80	19.0	0.90 M	0.90 M	0.90 M
4	-	100	-	-	0.06 M	0.06 M	0.06 M
5	-	94.1	5.90	-	0.07 M	0.07 M	0.07 M
6	-	76.2	4.80	19.0	0.82 M	0.82 M	0.82 M
No.	ACN	PC	DMSO	1,4-Di	[DI] ⁺ [Br] ⁻	[DI] ⁺ [BF ₄] ⁻	[DI] ⁺ [PF ₆] ⁻
7	100	-	-	-	0.60 M	0.60 M	0.60 M
8	94.1	-	5.90	-	0.60 M	0.60 M	0.60 M
9	76.2	-	4.80	19.0	0.70 M	0.70 M	0.70 M
10	-	100	-	-	0.07 M	0.07 M	0.07 M
11	-	94.1	5.90	-	0.09 M	0.09 M	0.09 M
12	-	76.2	4.80	19.0	0.12 M	0.12 M	0.12 M
No.	ACN	PC	DMSO	1,4-Di	[BMTA] ⁺ [I] ⁻	$[BMTA]^+[BF_4]^-$	$[BMTA]^+[PF_6]^-$
13	100	-	-	-	0.60 M	0.60 M	0.60 M
14	94.1	-	5.90	-	0.59 M	0.59 M	0.59 M
15	76.2	-	4.80	19.0	0.68 M	0.68 M	0.68 M
16	-	100	-	-	0.07 M	0.07 M	0.07 M
17	-	94.1	5.90	-	0.08 M	0.08 M	0.08 M
18	-	76.2	4.80	19.0	0.10 M	0.10 M	0.10 M
No.	ACN	PC	DMSO	1,4-Di	[DMPy] ⁺ [I] ⁻	$[DMPy]^+[BF_4]^-$	$[DMPy]^+[PF_6]^-$
19	100	-	-	-	0.50 M	0.50 M	0.50 M
20	94.1	-	5.90	-	0.50 M	0.50 M	0.50 M
21	76.2	-	4.80	19.0	0.60 M	0.60 M	0.60 M
22	-	100	-	-	0.02 M	0.02 M	0.02 M

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No.	ACN	PC	DMSO	1,4 - Di	[MPy] ⁺ [I] ⁻	[MPy] ⁺ [BF ₄] ⁻	[MPy] ⁺ [PF ₆] ⁻
23	-	94.1	5.90	-	0.05 M	0.05 M	0.05 M
24	-	76.2	4.80	19.0	0.08 M	0.08 M	0.08 M
No.	ACN	PC	DMSO	1,4-Di	[DMP] ⁺ [I] ⁻	$[DMP]^+[BF_4]^-$	$[DMP]^+[PF_6]^-$
25	100	-	-	-	0.15 M	0.15 M	0.15 M
26	94.1	-	5.90	-	0.15 M	0.15 M	0.15 M
27	76.2	-	4.80	19.0	0.10 M	0.10 M	0.10 M
28	-	100	-	-	0.02 M	0.02 M	0.02 M
29	-	94.1	5.90	-	0.09 M	0.09 M	0.09 M
30	-	76.2	4.80	19.0	0.14 M	0.14 M	0.14 M

Table 1. Cont.

^(a) The mole ratio (mol-%) of the V(acac)₃/N-heterocyclic aromatic electrolyte was 1/1. CAN = acetonitrile, PC = propylene carbonate, DMSO = dimethyl sulfoxide, 1/4-Di = 1/4-dioxane.

4. Conclusions

In this study, aromatic N-heterocyclic chemical salts $([MPy]^+[BF_4]^-, [MPy]^+[PF_6]^-, [DI]^+[BF_4]^-, [DI]^+[PF_6]^-, [BMTA]^+[BF_4]^-, and [BMTA]^+[PF_6]^-) and aliphatic N-heterocyclic chemical salts <math>([DMP]^+[BF_4]^-, [DMP]^+[PF_6]^-, [DMPy]^+[BF_4]^-, [DMPy]^+[PF_6]^-, [E-TEDA]^+[BF_4]^-, and [E-TEDA]^+[PF_6]^-) were synthesized and applied in an organic electrochemical capacitor as a supporting electrolyte. The synthesized aromatic and aliphatic N-heterocyclic chemical salts were confirmed successfully by ¹H-NMR, FT-IR, and GC/MS.$

The CV results for $V(acac)_3$ were found to be stable from -2.5 to 1.0 V when using electrolytes as aromatic N-heterocyclic chemical salts with acetonitrile. However, CV results were unstable or not detected when using electrolytes as aliphatic N-heterocyclic chemical salts with acetonitrile because the anion-exchange membrane was dissolved during the redox process. The electrochemical potential of V(acac)₃ was determined to be approximately 2.2 V under aromatic and aliphatic N-heterocyclic chemical salts (electrolytes) from its CV. The charge-discharge voltage distance of the $V(acac)_3$ in the acetonitrile electrolyte with the aromatic and aliphatic N-heterocyclic salts as supporters was 2.2 V; however, charge-discharge cycles could not be performed more than 20 times because the commercial membrane dissolved with the usage of acetonitrile electrolytes. In the solubility test with the vanadium complex, it was observed that the highest solubility was achieved in solvent mixtures with solvents of high donor numbers or higher polarizability, but chargedischarge profiles could not be obtained because the assembled commercial membrane dissolved in the electrolyte mixtures. From the above results, we conclude that the synthesized electrolyte supporters could be used as electrolyte additives in an electrochemical capacitor system.

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