

Distillable Ionic Liquids: Reversible Amide O Alkylation**

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Over the past three decades, ionic liquids (ILs) have stimulated significant scientific interest because of their appealing properties, structural diversity, and functional versatility, as well as an extensive range of existing and potential applications, such as reaction solvents, supporting electrolytes, functional materials, and many more.^[1] One of the main attractive features of ILs is their extremely low vapor pressure, which makes them distinct from and superior to the traditional volatile organic compounds (VOCs). This feature not only enables the applications that require high vacuum conditions, such as in situ XPS investigation,^[2] but also decreases the loss of solvents into the atmosphere and the risk of exposure, thus making it an environmentally preferable alternative to VOCs. However, an associated challenge is that the ILs cannot be easily recycled by means of simple distillation as in the case of VOCs, and thus severely limits their large-scale industrial applications.^[3] Up to now, efforts have been devoted to the study of the volatility or distillability of ILs.^[4–10] P. G. Jessop et al.^[4] developed a class of CO₂-switchable solvents, which can be switch back and forth between ionic and molecular forms by bubbling CO₂ and N₂, alternately, through the solution. The molecular forms enable facile separations of the high-boiling-point species from nonvolatile solvents.^[4c] Recent studies have revealed the presence of neutral ion pairs and ion aggregates in most ILs, and a measurable vapor pressure could be detected under vacuum and at elevated temperatures.^[5] Earle et al.^[6] first demonstrated the feasibility of vacuum distillation of aprotic ILs through vaporization of ion pairs at high temperature without decomposition. However, the low distillation rate, for example, 0.120 g h^{−1} for [EMIm]NTf₂ at 300 °C and 0.1 mbar,^[6] makes it very difficult for further application.^[7] Actually, the quaternization reaction for the synthesis of ILs is reversible with temperature, and a portion of the neutral precursors can be collected by thermal decomposition.^[8] More recently, the formation of the neutral acid and base precursors was found to occur readily in protic ILs through a proton-transfer mechanism.^[9] King et al.^[10] successfully regenerated protic ILs, which dissolved cellulose, by vacuum distillation of the neutral acid and base IL precursors at elevated temperatures, with a recovery rate up to 99.4 %.

In contrast, ILs are characterized by the flexibility in their design in relation to structure and function. The total number of possible ILs was estimated to be on the order of 10⁸, and their properties can be tailored by judicious selection of cation and anion species, and functional groups, to serve useful purposes.^[11] So far, several thousand ILs have been developed and studied, and most of the cation species are derived from the nucleophiles, such as imidazolium, quaternary phosphonium, and tertiary sulfonium, with electron-rich N, P, and S atoms as a strong nucleophilic centers. For the development of science and technology, there is always a need to design and create novel ILs. Recently, low-cost amide-cation-based ILs were developed and applied in liquid crystals,^[12] electrolytes,^[13] solvent extraction of metal ions,^[14] ionothermal carbonization of sugars,^[15] and more. Most of these amide-cation-derived ILs are Brønsted acidic, and the cationic precursors mainly include aliphatic amides and lactams (cyclic amides, e.g., caprolactam^[12]). However, there is still debate on whether the reaction of amides with H⁺ or other electrophilic reagents occurs at the amide nitrogen atom^[12,13a–c] or oxygen atom,^[13d,14,15] since the electron-withdrawing carbonyl group conjugated to the amide N tends to make the N less nucleophilic and the O more nucleophilic.

At the beginning of the present study, an attempt was made to answer the above question using the DFT/B3LYP method with the Pople 6-311 + G(d,p) basis set^[16] to fully optimize the amide DMF [(CH₃)₂NCHO] and its O- or N-alkylated products. The simulation results are summarized in Figures 1 and S1, and Tables S1 and S2 (see the Supporting Information). Since the n-π* electron delocalization in the N-C=O fragment (Figures 1, S1, and Table S1), DMF is essentially planar and the O (−0.62215 e) carries more negative charge than the N (−0.50138 e), thus indicating a higher nucleophilicity of the former. Additionally, the O-alkylated products are more stable than their N-alkylated congeners, with an energy difference of 13.29 kcal mol^{−1} for

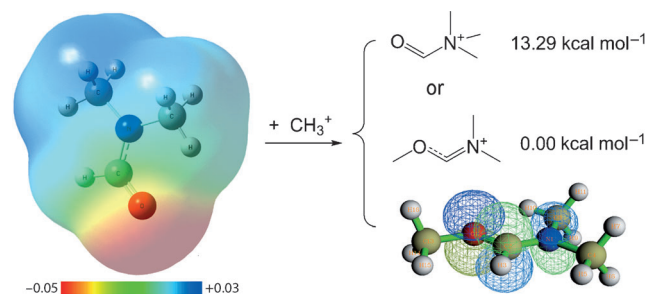


Figure 1. The color-coded electron density surface of DMF, its two possible methylated products and their relative energies, and the n-π* delocalization of the O-methylated product. The calculations were performed in the gas phase at the B3LYP/6-311 + G(d,p) level of theory.

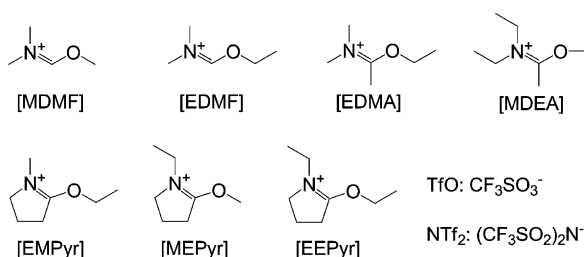
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the methylated DMF cation (Figure 1 and Table S2). In fact, the O-alkylated compounds maintain the basic conjugated system of amides, thus resulting in bond orders of 1.51 and 1.22 for N–C and C–O, respectively, for N⁺–C–O, and a second-order stability energy of 64.30 kcal mol^{−1} in (CH₃)₂N⁺CHOCH₃ (Table S2). As for the N-methylated DMF, the bond orders are 0.76 and 2.04 for the N⁺–C–O unit, and no n–π* delocalization was observed (Table S2). Similar results were also found for the ethylated DMF compounds (Table S2). Based on the higher nucleophilicity and more stable products, the amide O should be the position, or at least is the more favorable position, for the nucleophilic alkylation of amides with alkylating agents.

The above finding was further supported by our experimental results. As shown in Scheme 1, a series of O-alkylated-amide ILs were synthesized by the reaction of



Scheme 1. Structures and abbreviations of cations and anions used in this study.

amide with alkyl triflate (see the Supporting Information for details). This proposed structure was confirmed by ¹H/¹³C NMR spectroscopy. As illustrated for [MDMF]TfO (Figures 2a and b), both the ¹H and ¹³C NMR signals assigned to the three methyl groups do not coalesce but instead show greater separation, which exactly matches the N(CH₃)₂ asymmetry imposed by the C=N bond and the O–CH₃. The proton of the conjugated group N=C(H)–O appears at a high

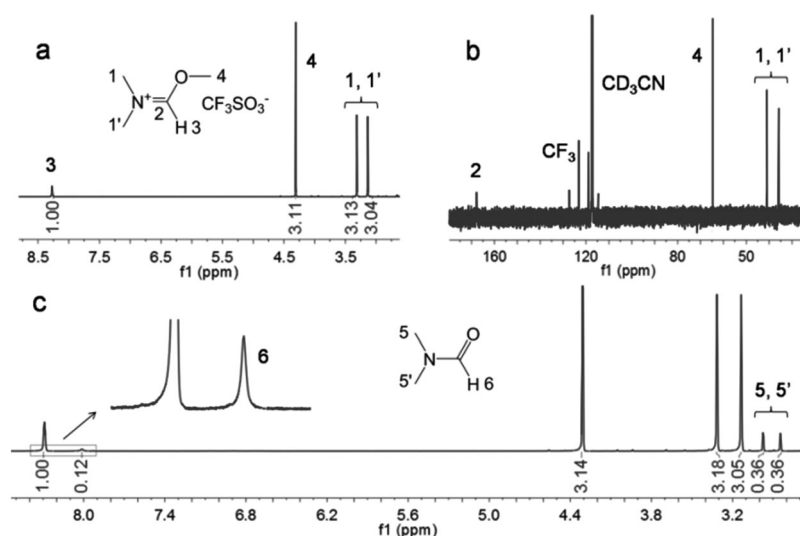


Figure 2. a, b) ¹H/¹³C NMR spectra of [MDMF]TfO in CD₃CN. c) ¹H NMR spectrum of the recycled [MDMF]TfO containing 11 mol % of DMF.

chemical shift of $\delta = 8.27$ ppm, thus implying its acidity. The quartet ($\delta = 127.36, 123.12, 118.87, 114.63$ ppm) in Figure 2b is characteristic of CF₃ in a TfO anion. Besides, NTf₂-based amide ILs were also prepared by anion exchange (see the Supporting Information for details) and characterized.

As a matter of fact, the amide O-alkylation reaction is readily reversible with temperature, and the ILs can revert to volatile molecular precursors (amide and alkyl triflate) at elevated temperatures. According to the TG curves shown in Figure 3, the decomposition temperatures of the TfO-based

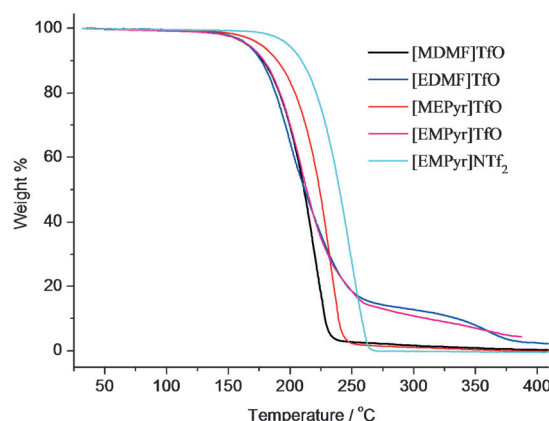


Figure 3. TGA curves of five ILs.

ILs (T_d at 5% mass loss) are around 170 °C, as listed in Table 1. The recovery of the amide ILs by distillation of the regenerated volatile precursors at elevated temperatures was first conducted for [MDMF]TfO, as detailed in Table 1. In a short-path vacuum (0.5 mbar) distillation apparatus, 8.0 g of [MDMF]TfO was added, and then the oil bath temperature was raised gradually. When heated to around 145 °C, the bubbles began to appear. At 210 °C, the steam distillate was collected in an ice/water bath within 10 minutes, thus giving 92 wt % of a liquid. NMR results revealed that the collected distillate contains only 87 mol % of [MDMF]TfO and 11 mol % of DMF (Figure 2c). The presence of DMF indicates that the distillation of [MDMF]TfO undergoes a process of amide O-dealkylation. After the addition of an equivalent of CF₃SO₃CH₃, the residual DMF could be completely converted into [MDMF]TfO, thus affording a recovery of 99 wt %, with a purity of up to 98 %. Since the boiling point of CF₃SO₃CH₃ is only 90 °C at atmospheric pressure, the DMF impurity in the distillate might arise from the volatility of CF₃SO₃CH₃ under vacuum. When the distillate was trapped in liquid N₂ (−196 °C), 99 wt % of [MDMF]TfO with a purity of 97 % could be recovered by vacuum distillation. This result demonstrates the feasibility of the direct recycling and reuse of ILs by the rapid distillation of the regenerated volatile precursors at elevated temperatures with no need for further processing.

Table 1: The recycling of the amide-cation-based ILs by vacuum distillation.

Entry	IL	$T_d^{[a]}$ [°C]	Vacuum degree ^[b] [mbar]	Cold trap T [°C]	Oil bath T [°C]	Recovery rate [wt %]	Purity ^[c] [mol %]	Amide content [mol %]	$[H^+]$ amide content ^[d] [mol %]
1	[MDMF]TfO	165	0.5	0	210	92	87	11	—
2	[MDMF]TfO		0.5	−196	210	99	97	—	—
3	[MDEA]TfO	179	0.5	−196	210	98	86		12
4	[MDEA]TfO		0.002	−196	175	98	89		9
5	[MEPyr]TfO	177	0.002	−196	175	98	90		8
6	[EDMF]TfO	165	0.5	−196	210	66	89		9
7	[EDEA]TfO	177	0.5	−196	210	65	77		21
8	[EDEA]TfO		0.002	−196	175	91	77		21
9	[EEPyr]TfO	171	0.5	−196	210	66	82		16
10	[EMPyr]TfO	166	0.5	−196	210	52	81		16
11	[EDMA]TfO	165	0.5	−196	210	67	81		16

[a] Decomposition temperature with 5 % mass loss. [b] By a Buchi vacuum pump V-700 with ultimate vacuum of 0.5 mbar or an Edwards RV12 vacuum pump with ultimate vacuum of 0.002 mbar. [c] Calculated from 1H NMR spectra. [d] Content of the O-protonated amide based on NMR analysis.

The distillation recovery of other samples was also studied (Table 1). These data are not as good as that for [MDMF]TfO. For example, only 66 wt % of [EEPyr]TfO was distilled (entry 9), thus leaving 28 wt % residue of O-protonated N-ethyl-2-pyrrolidone $[H^+EPyr]TfO$ (see Figures S3 and S4). And the distillate also contains 16 wt % of $[H^+EPyr]TfO$. Similar results were also obtained for other ethylated ILs (entries 6–11). The existence of a protonated amide should be related to the generation of H^+ during the O-ethyl elimination. For [MDEA]TfO and [MEPyr]TfO, though 98 wt % can be recovered, the crude distillates contain around 10 mol % of O-protonated amides. After crystallization in a mixture of diethyl ether and ethyl acetate, the overall recovery (purity: 98 %) was determined to be 70 wt % for [MDEA]TfO and 71 wt % for [MEPyr]TfO. Compared with other ILs, DMF derivatives (entries 1, 2, and 6) show better recovery ability with a smaller amount of impurities. This result may be related to the acidity of the $N=CH-O$ proton, which prevents the formation of $[H^+]$ from alkyl cations. When the vacuum pressure was decreased from 0.5 to 0.002 mbar, the distillation temperature could be reduced to 175 °C, and the recyclability could be enhanced to 91 wt % for [EDEA]TfO, with almost

the same purity. As for [MDEA]TfO, with a decrease from 0.5 to 0.002 mbar, the recovery rates were almost same and the purity was increased slightly from 86 mol % to 89 mol %. The high recovery rate of the methylated ILs relative to the ethylated ILs could also be observed from the TG results. As shown in Figure 3, the weight of the methylated ILs fell off gradually to about 0 %, while the curves for the ethylated ILs went through an inflection point at around 20 wt %.

For further and more extensive studies of these new ILs, their fundamental properties, such as melting point (T_m), crystallization temperature (T_c), density (ρ), surface tension (γ), conductivity (κ), viscosity (η), and electrochemical window (EW), were determined (Tables 2 and S3 in the Supporting Information), where appropriate. For the purpose of comparison, two 1-ethyl-3-methylimidazolium, [EMIm]-based ILs, which are one of the most commonly used ILs with low viscosity and high conductivity, were synthesized and characterized (Table 2). According to the solid–liquid phase transitions obtained from DSC measurements, all the amide-based ILs were shown to undergo both crystallization and melting processes, and many of them are liquids or subcooled liquids at room temperature with a T_m or T_c value of less than

Table 2: Basic properties of nine amide-cation-based ILs and two [EMIm]-based ILs.

Entry	IL	$T_m^{[a]}$ [°C]	$T_c^{[b]}$ [°C]	$\rho^{[c]}$ [g cm ^{−3}]	$\gamma^{[d]}$ [mN m ^{−1}]	$\eta^{[e]}$ [cP]	$\kappa^{[f]}$ [mS cm ^{−1}]	$EW^{[g]}$ [V]	$E_{cathodic}^{[h]}$ [V]	$E_{anodic}^{[i]}$ [V]
1	[MDMF]TfO	23.2	−6.95	1.4126	41.3	29.7	15.45	4.44	−1.62	2.82
2	[EDMF]TfO	−32.5	(−64.0)	1.3492	35.8	22.4	14.46	4.41	−1.61	2.80
3	[MEPyr]TfO	14.7	−27.4	1.3675	40.1	85.1	4.83	4.67	−1.87	2.80
4	[EEPyr]TfO	34.1	4.8	1.3165	35.1	52.3	6.15	4.62	−1.85	2.77
5	[MDMF]NTf ₂	37.6	−16.1	1.5405	36.2	29.3	10.96	4.41	−1.60	2.81
6	[EDMF]NTf ₂	2.9	(−60.7)	1.4946	34.9	21.6	11.29	4.47	−1.61	2.86
7	[EDMA]NTf ₂	33.1	11.3	1.4688	34.5	40.8	6.59	4.64	−1.83	2.81
8	[MDEA]NTf ₂	28.3	4.0	1.4469	35.1	66.9	3.48	4.63	−1.81	2.82
9	[EEPyr]NTf ₂	29.0	10.0	1.4460	35.1	33.7	6.10	4.62	−1.88	2.74
10	[EMIm]NTf ₂			1.5182 ^[j]	39.0 ^[k]	32.0 ^[l]	8.96 ^[m]	4.56	−2.18	2.38
11	[EMIm]TfO			1.3850	41.9 ^[o]	43.6	9.27	4.43	−2.18	2.25

[a] Melting point. [b] Crystallization temperature (cold crystallization in brackets). [c] Density at 25.0 °C. [d] Surface tension at 25.0 °C. [e] Viscosity at 25.0 °C. [f] Conductivity at 25.0 °C. [g] Electrochemical windows. [h] Cathodic potential limit. [i] Anodic potential limit. [j] Literature value, 1.519 g cm^{−3}.^[17] [k] Literature value: 41.62 mN m^{−1}.^[18] [l] Literature value: 32.6 cP.^[17] [m] Literature value: 9.1 mS cm^{−1}.^[17] [o] Literature value: 44.46 mN m^{−1}.^[18]

25 °C. The cold-crystallization behaviors and lower T_m values (entries 2 and 6) of the two [EDMF]-based ILs suggest that this cation is less prone to form an ordered structure than others. The densities (ρ) of the ILs fall in the range from 1.3165 to 1.5405 g cm⁻³ at 25 °C, densities which are close to those of [EMIm]-based ILs. For a given anion, the amide-derived ILs exhibit a lower surface tension (γ , 34.5–41.3 mN m⁻¹, 25 °C) than [EMIm] ILs, for example, 41.9 mN m⁻¹ for [EMIm]TfO.

The viscosities (η) of the ILs were measured at 25 °C and the results are listed in Table 2. Accordingly, the amide-derived ILs are generally of low viscosity, with values as low as 21.6 cP for [EDMF]NTf₂, which is even less viscous than [EMIm]NTf₂ (32.5 cP). Such low viscosity can be related to the structures of the amide cations, which are of (quasi)planar geometry, low symmetry, and contain an ether moiety (Scheme 1). These structural features are useful for decreasing the ion packing efficiency and offer more free volumes for promoting mass transfer.^[19] The viscosity values are generally governed by three major factors: the amide precursor, the O-alkyl chain length, and anionic species. First of all, compared with other ILs (e.g., [EDMA]NTf₂: 40.8 cP), DMF-derived ILs are the least viscous (e.g., [EDMF]NTf₂: 21.6 cP). This result can be attributed to the hydrogen atom on N=CH–O, with reference to imidazolium ILs, where the small C2–H atom on the cation ring allows more rotational freedom of the N-alkyl chains for low viscosity.^[19a] Secondly, the amide O-bonded alkyl chain result in an ether group. Ether moieties are featured for their ability to reduce the liquid viscosity, and the O-terminal rodlike CH₂CH₃ tail is much more efficient in reducing viscosity than the spherical CH₃ tail. Our experimental results are in complete accordance with the relevant literature,^[19b] and the O-ethyl ILs are much less viscous than O-methyl ILs, for example, [EEPyr]TfO (52.3 cP) versus [MEPyr]TfO (85.1 cP). Thirdly, by keeping the anion constant, most TfO ILs are much more viscous than NTf₂ ILs, as expected.^[17] However and interestingly, DMF-derived TfO ILs are nearly as low in viscosity as NTf₂ ILs, for example, [EDMF]TfO (22.4 cP) versus [EDMF]NTf₂ (21.6 cP). In addition, this unusual result can also be observed in the following conductivity values.

Generally, low viscosity allows high conductivity for ILs and thus they serve as better electrolytes in electrochemical devices. The conductivities (κ ; Table 2) of the samples that are (supercooled) liquids at 25 °C were investigated, and ranged from 3.48 to 15.45 mS cm⁻¹. Clearly, the overall relatively high conductivity values benefit from the low viscosity. These DMF-derived ILs are even more conductive than their [EMIm]-based counterparts, for example, [EDMF]NTf₂ (11.29 mS cm⁻¹) versus [EMIm]NTf₂ (8.81 mS cm⁻¹). Another major factor in determining conductivity is ionic size, of which the small sizes are convenient for ion transfer. For a given cation, although TfO-based ILs are generally more viscous than NTf₂-based ILs, the former are more conductive than the latter, especially for DMF derivatives. For example, for [MDMF]TfO (15.45 mS cm⁻¹) versus [MDMF]NTf₂ (10.96 mS cm⁻¹), the former is nearly as low in viscosity as the latter, but is smaller in size than the latter.

The electrochemical windows of the neat ILs were studied by cyclic voltammetry (CV) on a glassy-carbon electrode, as illustrated in Figure S2 in the Supporting Information. Table 2 summarizes the test results for the cathodic (E_{cathodic}) and anodic (E_{anodic}) limits, and the overall electrochemical windows ($\text{EW} = E_{\text{anodic}} - E_{\text{cathodic}}$). As can be seen, all of the amide-derived ILs possess a relatively wide electrochemical window, ranging up to approximately 4.5 V, which is much larger than the protic amide ILs (ca. 2.2 V),^[13a] and comparable to [EMIm]-based ILs (ca. 4.5 V, Table 2). Compared to [EMIm] ILs ($E_{\text{anodic}} \approx 2.3$ V for NTf₂ and TfO), the anodic limit, related to the oxidation of anions, of the amide-based ILs is more positive (ca. 2.8 V). So although the cathodic limit of the latter (ca. –1.7 V) is less negative than that of the former (ca. –2.2 V), their overall electrochemical windows are almost equal. This difference in the E_{anodic} value suggests that counterions may exert a significant effect on the electrochemical stability of each other, although it was generally assumed that the cathodic limit is set by the reduction of the cations and the anodic limit is set by the oxidation of the anions.^[20] Besides, the cathodic limits of DMF derivatives are a bit less negative (ca. –1.6 V), and should be related to the acidity of the N=CH–O proton, analogous to imidazolium ILs.^[19a] The combination of the wide electrochemical window and high conductivity implies a potential application in electrochemistry.

In conclusion, we present the synthesis of a new class of low-cost amide-derived aprotic ILs from amide O-alkylation with alkyl triflate. The amide O-alkylation reaction is readily reversible with temperature, and the regenerated volatile precursors can be easily vacuum distilled at about 200 °C and also revert to ILs at room temperature, with the maximum recovery rate of up to 99 wt % and purity of 97 %. To our knowledge, this is the first case demonstrating the feasibility of the easy recycling of aprotic ILs by the distillation of the regenerated molecular precursors at elevated temperatures without the need for further processing. We believe that this synthesis strategy can be extended to designing and developing new ILs and other useful compounds, and the recycling strategy can be applied to solving the recycling challenge of the nonvolatile ILs in large-scale applications. Besides, the amide-cation-based ILs have low viscosity (21.6 cP at 25 °C), high conductivity (15.45 mS cm⁻¹ at 25 °C), and wide electrochemical windows (ca. 4.5 V), thus indicating their potential in electrochemical applications.

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