

Electrodialytic Universal Synthesis of Highly Pure and Mixed Ionic Liquids

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Cite This: *ACS Omega* 2022, 7, 21925–21931

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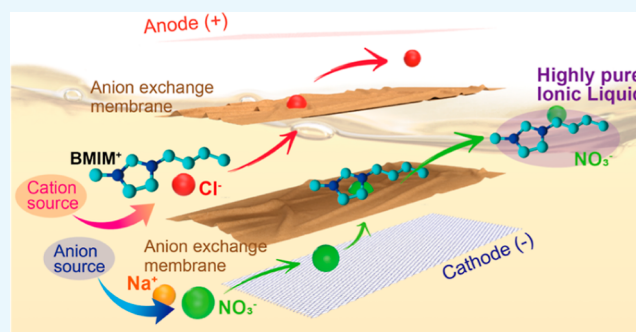


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Supporting Information

ABSTRACT: Ionic liquids (ILs) have attracted significant attention from researchers in various fields as a result of their unique properties. As new and important applications are identified for these materials, there is also a drive to develop methods for accessing a wider range of ILs. However, despite this demand, only a few techniques have so far been reported and, more importantly, general but efficient processes for IL synthesis have been lacking. Thus, it would be beneficial to devise a cost-effective, environmentally friendly means of producing a wide variety of pure ILs. The present work demonstrates a general purpose electro dialysis approach to the formation of highly pure ILs, based on the formation of nine different ILs from various combinations of cations and anions. In each case, the IL is obtained with a purity of greater than 99%. This method offers the advantages of avoiding the use of hazardous organic solvents and eliminating tedious and costly purification processes. Unlike conventional methods, this membrane-based technology also prevents the generation of side products. Mixed ILs have many potential applications, and the present technique readily generates various mixed ILs based on a simple adjustment of the applied current.



1. INTRODUCTION

Ionic liquids (ILs) are salts composed of organic cations combined with inorganic or organic anions and having melting points at or below 100 °C.^{1,2} ILs have emerged as a very important class of materials because of their unique physicochemical properties, including high boiling points, superior thermal and electrochemical stabilities, negligible vapor pressures, lack of flammability, wide electrochemical windows, and ability to act as solvents or electrolytes.^{3–5} As a result of these characteristics, these liquids have applications in electrochemistry^{6,7} and as solvents,^{8–10} engineering materials,^{11,12} catalysts, and biomedical materials.^{13–15} An obvious advantage of ILs over traditional organic solvents is that their properties can be finely tuned by changing the combination of cations and anions or even making minute changes to the cation or anion moieties. Based on the numerous cations and anions that could potentially be incorporated into ILs, it has been estimated that 10¹⁸ ion pairs are possible.¹⁶

Despite the significant potential of ILs, the purity of these materials remains a critical issue. Takao and Ikeda pointed out that different batches of the same IL prepared separately can exhibit varying physical properties as a consequence of small changes in the amount and type of impurities that are present in each specimen.¹⁷ Thus, it is very important to produce pure ILs so as to obtain specific physicochemical properties.¹⁸ It has been reported that trace level impurities in ILs can greatly affect their physicochemical characteristics and so modify reaction mechanisms and kinetics,¹⁹ energy storage capaci-

ties,²⁰ spectroscopic behaviors, electrochemical properties, and catalytic activities.^{21,22}

To date, ILs have been synthesized using either of two primary methods. In one approach, amines, phosphines, or sulfides are reacted with acids to produce protic ILs or with alkyl halides to give alkylated ILs. In the other approach, the alkylation does not generate an IL and so the counteranion to the ammonium, phosphonium, or sulphonium ion must be exchanged with a suitable anion to obtain the desired IL. This method is referred to as anion metathesis and is currently the most widely used means of producing ILs because it allows for a diverse range of ions and can be scaled up to produce bulk amounts of ILs.^{23,24} However, the ion metathesis technique suffers from a serious drawback in that a stoichiometric amount of side products is also generated, such that one or more additional purification steps are required. These purification processes can be labor-intensive and may not remove all impurities. The use of silver salts can eliminate this problem, but adds to the cost of the process and only removes halide impurities from hydrophilic ILs. As an alternative, the IL

Received: April 8, 2022

Accepted: June 3, 2022

Published: June 14, 2022



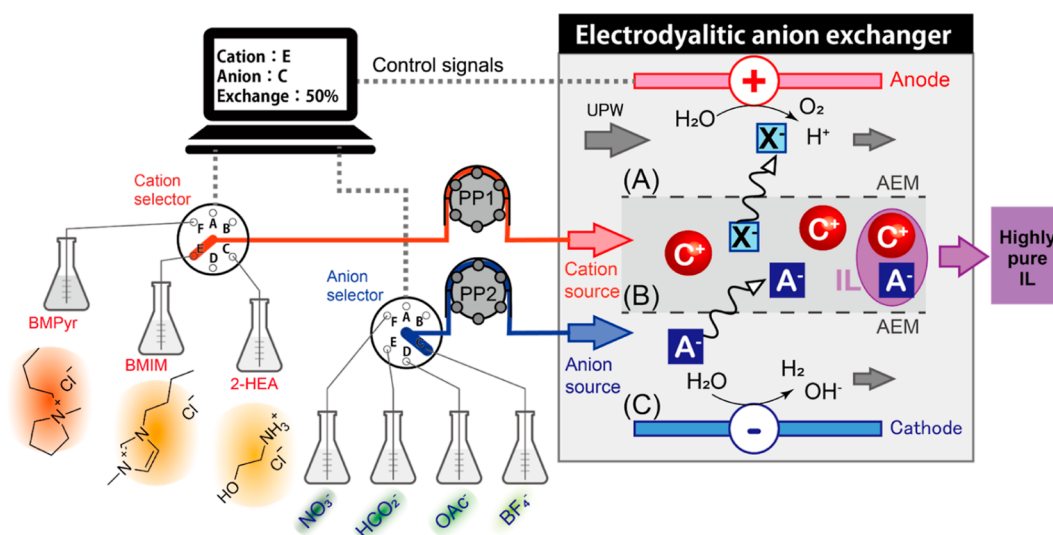


Figure 1. Electrodyalytic apparatus used to synthesize ILs. A, B, and C mean channels Ch-A, Ch-B, and Ch-C, respectively.

can be passed through an ion exchange column. This technique has provided a very high level of purity in some cases, but is extremely slow and non-continuous while requiring a large amount of resin and frequent regeneration.^{25–27}

Electrodialysis (ED) is a separation process, in which ions are passed through an ion exchange membrane in response to the effect of an applied electromotive force.²⁷ Cations and anions can be combined using this technique as a means of producing ILs. ED could therefore generate ILs without requiring an additional purification process. Himmler et al. reported an electrodyalytic IL synthesis using a bipolar membrane to generate 1-ethyl-3-methylimidazolium hydroxide ([EMIM][OH]) from [EMIM] ethyl sulfate ([EMIM]-[EtOSO₃]) as a precursor, followed by neutralization using different acids.²⁷ The batch production of ILs via this process gave high purities ranging from 98 to >99%. Haerens et al. and Meng et al. also demonstrated the synthesis of ILs using modified batch ED processes.^{28,29} This prior work employed cation and anion exchange membranes (AEMs) to combine cations and anions in an acceptor, albeit with low purities of approximately 95%. It was concluded that the purity of the final product was greatly affected by the purity of both the cation and anion sources. Although these data suggest that the use of pure precursors to synthesize ILs via ED could generate highly pure products, there appear to have been only three reports of the electrodyalytic synthesis of ILs over the last 15 years. On the other hand, the electrodyalytic impurity removal and recycling ILs were reported. The impurity removal was based on the different mobility under the electric fields. The impurities such as Na⁺ and Cl⁻ are more rapidly transferred than cations and anions, which are consisting of ILs.³⁰ The recycling of ILs with ED is also reported. Ion-consisting ILs are transferred from the used to other IL solution to enrich the targeted ILs.^{31,32} In these recycling procedures, the obtained IL recovery is not so high (~90%) even though the solutions were circulating into the ED device.

The present work reports the in-line production of highly pure ILs (greater than 99% purity) using a modified and very simple electrodyalytic approach in conjunction with halogenated precursors. This method is able to use cations and anions having a wide range of sizes and polarities. The synthesis can

be achieved with one passing through ED device consisting effective thin solution layers. Mixed ILs are currently utilized in important applications such as supercapacitors, and the present technique could potentially be used to produce such mixtures. Varying the current in this process provides a simple means of changing the anion amounts to produce ILs having specific anion compositions.

2. METHODS AND MATERIALS

2.1. IL Synthesis Using an Electrodyalytic Anion Exchanger.

The chemicals used in this work are summarized in Table S1 in the Supporting Information. All aqueous solutions were prepared with deionized water produced using an RF000220 apparatus (www.advantec.com).

A specially designed three-layered electrodyalytic anion exchanger (EAE) was fabricated for IL synthesis. Figures 1 and S1 in the Supporting Information present diagrams of this equipment. Three semimicro solution channels were prepared on poly(vinyl chloride) plates by milling the plates to a thickness of approximately 0.2 mm and employing a 0.13 mm thick gasket. Each gasket used in this work was prepared by affixing a Teflon mesh with a sieve opening size of 204 μm and a thickness of 100 μm (F-3220-04, www.flon-ind.com) onto a parafilm template by heating at 40 °C while applying 0.6 MPa pressure for 20 min. A channel was also formed on the parafilm template using a CO₂ laser cutter (Beamo, flux-japan.jp) prior to applying the mesh. The active channel was 5 mm wide and 40 mm long. Platinum mesh electrodes were subsequently attached to the solution channel on each poly(vinyl chloride) plate, and these electrodes were electrically connected using stainless steel rods. These channels were subsequently separated with AEMs (Figure 1, SELEMION AMVN, [www. agec.com](http://www.agec.com)).³³ Similar electrodyalytic devices were used for ion transfer in our previous works.^{34–36}

2.2. Flow System for IL Synthesis.

The solution flow through the experimental apparatus is also shown in Figure 1. In this system, the cation solution was pumped through 0.5 mm inner diameter tubing (Pharmed) into the center channel (Ch-B) of the EAE at a rate of approximately 0.4 mL/min using peristaltic pump PP1 (MP-2000, ssl.eyela.co.jp). The inlet of PP1 was connected to a selection valve (C25-3184EMH, vici.com) to allow several different cation solutions

to be selected. Similarly, an anion solution was pumped into the cathode side (Ch-C) of the EAE at 1.75–3.5 mL/min through 1.5 mm inner diameter tubing (Pharmed) using another peristaltic pump (Gilson mini pulse III, www.gilson.com) in conjunction with another selection valve. Purified water (UPW) was pumped into the anode side channel (Ch-A) via a Unimol pump (UPS-112E, www.nitto-kohki.co.jp) at 3.0 mL/min. The dc power for the EAE was supplied by a PA36-1.2B unit (www.texio.co.jp) operating in the constant current mode. The selection valves and dc power supply were computer controlled.

2.3. Synthetic Procedure. A cation source solution was pumped through the central acceptor channel, Ch-B (Figure 1), at a flow rate of 0.4 mL/min. Anion source solution was pumped through Ch-C. Ultrapure water (UPW) was flowed through Ch-A using another pump at a flow rate of 3.0 mL/min. An electrical current was applied to the EAE device. The system was kept flowing for 10 min to reach equilibrium. Then, the production solution, which was the effluent of the Ch-B (Figure 1), was collected and analyzed for cations and anions using ion chromatographs for the evaluation. The flow rate of the Ch-A was controlled for the quantitative conversion if required. Only some differences in the used parameters were used depending on the differences in used cations and anions, which are summarized in Table S2 in Supplementally Information.

2.4. Evaluation of Synthesized ILs. The purity and yield of each IL were evaluated by ion chromatography using Shodex IC YS-50 (4.6 mm × 125 mm) and Shodex IC SI-90 4E (4.0 mm × 250 mm) columns for the analysis of cations and anions, respectively. Prior to anion analysis, the IL solution was passed through a solid-phase extraction cartridge (Slim-J SCX 500 mg, www.gls.co.jp) to remove cations from the sample so as not to damage the anion separation column. The details of the chromatographic analyses are summarized in Table S3.

3. RESULTS AND DISCUSSION

3.1. Electrolytic IL Synthesis and Parameter Optimizations. The present study synthesized ILs using the widely studied cations 1-*n*-butyl-3-methylimidazolium (BMIM⁺), 2-hydroxyethylammonium (2-HEA⁺), and 1-butyl-1-methylpyrrolidinium (BMPyr⁺) to demonstrate the electro-dialytic anion exchange process. The chloride salts of these cations were employed as the cation precursors, while the anions NO₃⁻, HCO₂⁻, OAc⁻, and BF₄⁻ were supplied as sodium or lithium salts. Anion salts were used rather than the corresponding acids because they could be obtained in highly pure form and were more stable, less volatile, and non-reactive.³⁷ The application of anion salts to the synthesis process was vital to the preparation of highly pure ILs in this work. The nine ILs shown in Figure 2 were synthesized based on combinations of these cations and anions to demonstrate the effectiveness of the present method.

Initially, the possibility of IL synthesis using the EAE device was assessed by generating [BMIM][NO₃] (IL1), having a melting point of 17.7 °C, using [BMIM][Cl] as the cation source. In this process, the original Cl⁻ anions were removed and replaced with NO₃⁻, after which the concentrations of Cl⁻ and NO₃⁻ in the product were determined by ion chromatography (Figure S2). During ED, the extent of ion transfer is dependent on the electrical current that is applied, and the effect of the electrical current in the present work is

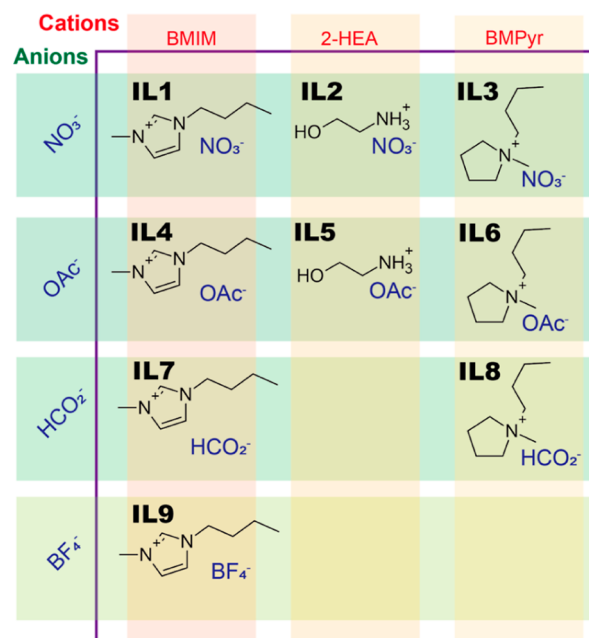


Figure 2. ILs synthesized in the present study.

shown in Figure 3a. With increases in the electrical current, the concentrations of Cl⁻ and NO₃⁻ were, respectively, decreased and increased in the outgoing production solution. The optimal performance, as reflected by a [NO₃⁻]/[BMIM⁺] ratio

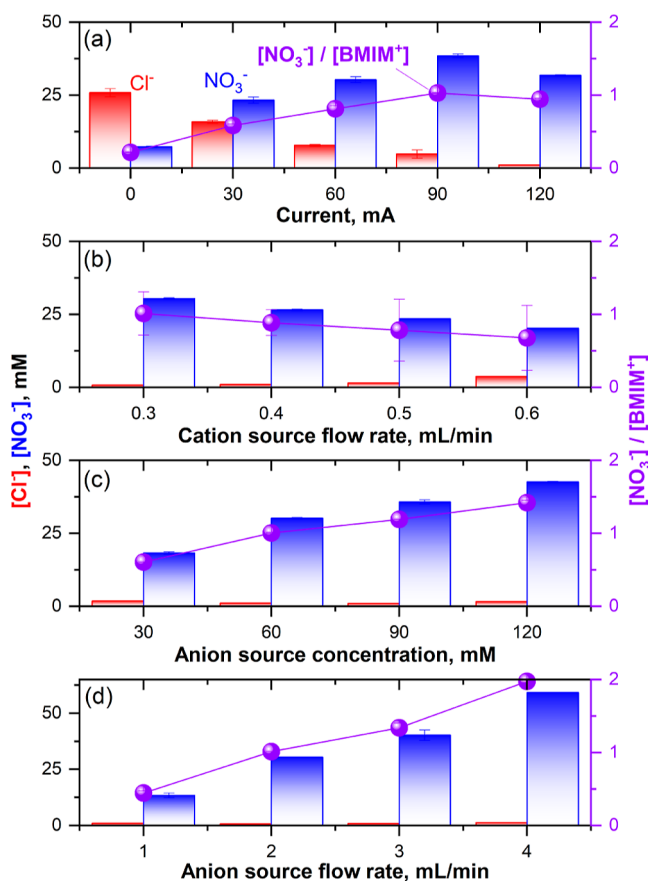


Figure 3. Effects of the experimental parameters. Details of the experimental conditions are presented in Table S4.

of approximately 1, was obtained at 90 to 120 mA. Using a cation source concentration of 33.6 mM with a flow rate of 0.40 mL/min, complete anion replacement would theoretically require a current of 21.6 mA. Thus, even though the anion source flow provided a sufficient Cl^- supply of 180 $\mu\text{mol}/\text{min}$ (based on an anion concentration of 60 mM and a flow rate of 3 mL/min) relative to the $[\text{BMIM}]$ supply of 13.4 $\mu\text{mol}/\text{min}$, the current efficiency was only 18% at 120 mA. This poor efficiency is attributed to migration of some of the NO_3^- introduced into the cation source flow (Ch-B) to the UPW flowing through the anode channel (Ch-C). The transfer efficiency of NO_3^- ions through an anion exchange membrane is greater than that of chloride ions,^{38,39} and, as a result, the complete (>99%) removal of Cl^- ions required a current of 120 mA during these trials. The other parameters were also optimized throughout these experiments. A higher cation source solution (Ch-B) flow rate was found to reduce the extent of Cl^- removal as well as the $[\text{NO}_3^-]/[\text{BMIM}^+]$ ratio at a current of 120 mA, indicating that this current was insufficient for that flow rates (Figure 3b). However, it was difficult to increase the current above this value because the resulting high current density (greater than 0.06 A/cm², equivalent to 3 W at approximately 25 V and 0.12 A) would have raised the device temperature as a result of Joule heating³⁴ and so possibly damaged the membrane during prolonged use. Increasing either the anion source concentration (Figure 3c) or flow rate (Figure 3d) increased the $[\text{NO}_3^-]/[\text{BMIM}^+]$ ratio above 1, indicating that too many anions were transferred to the cation source solution. Both BMIM^+ and H^+ were present in the cation source solution as counterions to the anions. H^+ were generated as a consequence of autoprotolysis in response to the electric field, with the corresponding OH^- ions being transferred to the purified water in the anode channel via the anion exchange membrane. This effect was confirmed by the lower pH of the cation source solution at higher anion source flow rates and concentrations. On the basis of these trials, a current of 120 mA, a cation source flow rate of 0.40 mL/min, and an anion source concentration of 120 mM were selected as optimal. The anion source flow rate was adjusted to obtain quantitative anion conversion using the different anions. Employing the present method, IL1, IL2, and IL3 were successfully synthesized, and the anion chromatograms of these products are presented in Figures S2–S4. Furthermore, the cation chromatograms for IL1, IL2, and IL3 are shown in Figure S5. The cations supplied as source solutions are remained in products without any losses. In each case, the purity of the product based on the anion concentration was in excess of 99%.

3.2. Weak Acid Anion Sources. Using the optimized conditions described in Section 3.1, ILs were synthesized with weak acids. These anions were introduced as their lithium salts to avoid contamination with the cations contained in anion sources. Lithium ions were used because these ions have the largest hydration radius among the alkaline metal ions and thus undergo the least amount of diffusion. The data indicate that a quantitative exchange of Cl^- for OAc^- could not be achieved using 120 mM LiOAc (Figure 4). During operation of the unit, the electrolysis of water in the anion source channel (Ch-C) generated OH^- ions. These ions had a higher electrophoretic velocity than OAc^- ions such that the former ions were transferred instead of OAc^- . As the result, the pH values of the effluent product and anion source solutions were increased to 12.22 and 12.28, respectively.

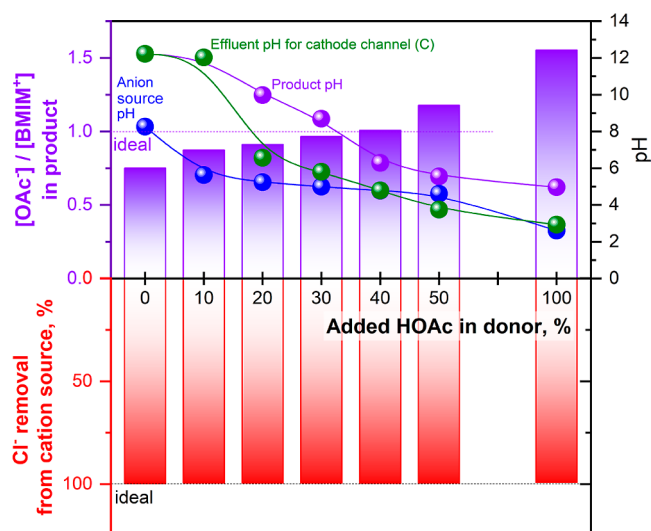


Figure 4. Effect of the proportion of the anion present in the acidic form.

As a means of mitigating this issue, a 120 mM HOAc solution was instead used as the anion source. The conductivity of this solution was too low to permit the use of a current of 120 mA with the power supply employed in this work (which had a maximum voltage of 35 V dc) and so the current was changed to 80 mA. Even at this lower electrical current, a $[\text{OAc}^-]/[\text{BMIM}^+]$ ratio of approximately 1.55 was obtained. The acidic anion source solution also inhibited OH^- generated by water electrolysis on the cathode surface with neutralization. However, the concentration of OAc^- transferred into the product stream exceeded that of BMIM^+ obtained from the cation source because of the effect of autoprotolysis in the cation source channel (Ch-B), as discussed above. A trial was also performed using a mixture of LiOAc and HOAc (72 mM LiOAc/48 mM HOAc) as the anion source, and this experiment gave an $[\text{OAc}^-]/[\text{BMIM}^+]$ ratio of 1 (Figure 4). Thus, this mixture of the Li salt and the acid form was used as the anion source in subsequent trials.

3.3. Application to Universal IL Synthesis. Using the optimized protocol, nine ILs were synthesized with the present method. The purity of each material was evaluated by ion chromatography and the concentrations of ions in these products are summarized in Figure 5. It is evident that the desired cation was present in each IL at a concentration in excess of 99%. In addition, the original Cl^- anions were replaced with the target anions with efficiencies of $99.1 \pm 0.4\%$ for all ILs synthesized in the present study. Consequently, the purities based on anion concentrations were $99.0 \pm 0.3\%$ for all ILs. The impurities identified in the products are summarized in the top panel of Figure 5, from which it is apparent that small amounts of Cl^- ions remained ($<0.87 \pm 0.31\%$). However, this residual Cl^- was found to decrease further in an experiment, where we removed water to produce water-free IL using a smart evaporator (C1, biochromato.com) from our production IL solution. In this process, drying air was circulated with purification by a column filled with activated charcoal. This procedure decreased the Cl^- concentration in the IL from 0.27 to 0.08 mM, while increasing the purity to 99.3%. Note that fluoride was observed in IL9 because the BF_4^- anions were readily decomposed under the acidic conditions to generate F^- .

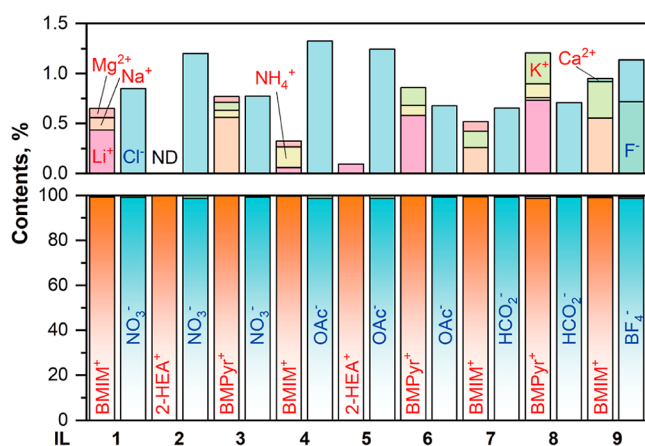


Figure 5. Ions found in the synthesized ILs, calculated as the ratio of each ion concentration to the total ion concentration. ND: not detected.

Several different cations were found in the products, depending on those in the cation source solution, and cation impurities were also identified. Thus, it is important to employ a highly pure cation source when using this anion exchange method. However, only one form of pure cation source is required in the present method.

3.4. Mixed IL Synthesis. Recently, mixed ILs have been investigated^{40,41} because these materials may have special applications, such as in supercapacitors.⁴² In the present method, the conversion efficiency could be controlled by adjusting the applied current, and so this system was assessed as a means of obtaining mixed ILs (Figure 6). Specifically, the proportions of Cl^- and NO_3^- in the product were varied by changing the applied current, confirming that mixed ILs having specific ion ratios could be synthesized simply by modifying the current.

4. CONCLUSIONS

This work demonstrated the use of ED-mediated IL synthesis as a versatile approach to the production of high-purity ILs. This system was able to generate nine ILs from hydrophilic and hydrophobic ions having a range of ions and sizes, thus confirming its versatility. ILs could be obtained from the salts of strong and weak acids. The present work investigated to access a variety of ILs with high purity without the need for cumbersome purification steps. The present method does not produce side products or has no problems such as incomplete reactions that leave extra impurities in the final product. Rather, appropriate control of the conditions can mix a stoichiometric amount of anions and cations minimizing the chance of introducing impurities. This newly developed technology does not use organic solvents and so also has a lower environmental impact. Finally, numerous materials can be employed to access the same IL. Also, the present method can combine seemingly numerous anions and cations to provide a wide number of ILs. All these factors indicate that this technique provides a highly general means of generating ILs having purities greater than 99% and has significant potential as a continuous in-line system.

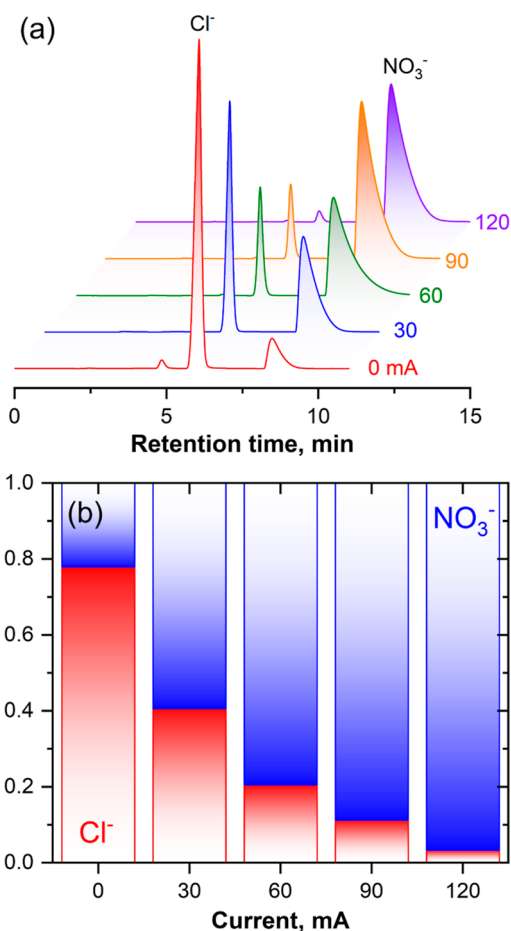


Figure 6. Compositions of mixed ILs obtained at various applied currents. (a) Anion chromatograms of ILs obtained with different applied currents. (b) Anion molar ratio for ILs with different applied currents.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02209>.

Chemicals used in the present study; structure of EAE; summary of the synthesis conditions; separation conditions for ion chromatography; chromatograms of ILs 1, 2, and 3; and optimization parameters (PDF)

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Notes

The authors declare no competing financial interest.

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