Chapter

Production of 1-Butyl-3-Methylimidazolium Acetate [Bmim][Ac] Using 1-Butyl-3-Methylimidazolium Chloride [Bmim]Cl and Silver Acetate: A Kinetic Study

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Abstract

Since most of the literature alternatives used to produce the ionic liquid 1-butyl-3-methylimidazolium acetate [Bmim][Ac] are very slow and require different solvents, we have used in this work a new process to produce the [Bmim][Ac] by the reaction of the ionic liquid 1-butyl-3-methylimidazolium chloride [Bmim]Cl with silver acetate (AgAc) where silver chloride (AgCl) precipitates as a by-product. The genuine experimental work and kinetic analyses presented here indicate that the reaction rate constant $k = 7.67\text{x}10^{12}\ e^{(-79.285/RT)}$. That is, the Arrhenius constant $k_o = 7.67\text{x}10^{12}$ L/mol.s and the activation energy $E_a = 79.285$ kJ/mol. The very high value of the Arrhenius constant indicates that the reaction of [Bmim]Cl with silver acetate to produce [Bmim][Ac] and silver chloride is extremely fast.

Keywords: ionic liquids, production, 1-butyl-3-methylimidazolium acetate [Bmim][Ac], 1-butyl-3-methylimidazolium chloride [Bmim]Cl, silver acetate, silver chloride, kinetic study

1. Introduction

The last two decades has witnessed a growth in the research activities related to ionic liquids (ILs). Most of the work focus on replacing the widely used volatile organic solvents (VOCs) by suitable alternative solvents with minimum chemical waste and environmental pollution. The readily available VOCs have some ecological constraints such as high volatility, fire hazardous, risk explosion, and toxicity that force researchers to develop better and safer solvents.

In general, ILs are in liquid state at below 100 °C and possess negligible vapor pressure [1–4]. They have gained more applications nowadays as an important class of non-toxic, non-volatile, environmentally-friendly solvents in

(bio)catalysis —applicable to many ionic, polar and nonpolar structure groups— and as efficient electrolytes [5]. In addition, ILs are good solvents for a wide range of inorganic and organic materials, have high thermal stability, high ionic conductivity and easy recyclability; these are some reasons to consider ionic liquids as "green solvents" [5]. The increased interest in ILs since 1990 is clearly due to the realization that these materials, formerly used for electrochemical applications including electrolytes for batteries, capacitors and charge storage devices as well as in the area of biomass utilization [6].

The ionic liquid of interest in this work is the 1-butyl-3-methylimidazolium acetate [Bmim][Ac], which has a low vapor pressure, hydrophilic, and is considered as one of the emerging important ILs in the solvent industry which has some promising applications as a solvent for lignin. This IL is produced as a reagent mainly in United States, Germany, France, and China. The current price of 1 kg of [Bmim][Ac] IL is about 785 EUROS [7, 8].

In this work, we will try to select the most feasible process alternative among the others to produce [Bmim][Ac] ionic liquid. Then to experimentally determine the kinetic data necessary to design a continuous stirred tank reactor (CSTR) for the production of [Bmim][Ac] based on the selected process, i.e. to determine the rate equation of the reaction and its order with respect to both reactants, the rate constant (k) as a function of temperature, and the activation energy of the reaction (E_a).

2. Uses of [Bmim][Ac]

There are several needs related to the [Bmim][Ac] ionic liquid and has many advantages over conventional organic solvents used nowadays due to it significantly low vapor pressure and relatively high solubility. Although [Bmim][Ac] is not a widely available product, it is preferred over other solvents in the extraction of lignin; the primary natural polymer found in wood [2].

Different ionic liquids, containing the $Bmim^+$ cation, are able to efficiently dissolve cellulose. However, the ability of ILs to truly dissolve cellulose is significant when cellulose derivatization is attempted. A series of experiments on etherification (carboxymethylation) of cellulose was performed by [9] using both the conventional suspension approach (slurry) with 2-propanol as the principal reaction media and a totally homogenous reaction approach using ionic liquids as a reaction media capable of dissolving cellulose.

Upon a totally homogenous etherification, the [Bmim][Ac] ionic liquid was found to give the highest degree of substitution. The product obtained was water-soluble and had a degree of substitution (DS) of 0.59. The substitution pattern of the products obtained from the homogenous reactions follow the same substitution pattern as the products obtained from the conventional suspension process. This indicates that the properties of the products are in line with products prepared via the conventional reaction route [9].

Low solubility and undesirable denaturation in conventional solvents still represent a significant challenge for efficient extraction, accurate characterization and multipurpose processing of collagen, which is important in fighting the visible effects of aging on the skin. [Bmim][Ac] was evaluated as an alternative solvent for type I collagen [10]. Real-time polarizing optical microscope observation indicated complete disintegration of hierarchical structure of collagen aggregates as solubilized in [Bmim][Ac] at 25 °C where the solubility reached 8.0 wt.%; > 10 times higher than that in conventional dilute acetic acid. The high solubility of collagen in [Bmim][Ac] at 25 °C is ascribed to the loose binding between $[Bmim]^+$ and

$[CH_3COO]^-$, as well as stronger proton-accepting ability of the [Bmim][Ac], which enabled rupture of those intermolecular hydrogen bonds and the ionic bonds that stabilized the collagen aggregates. However, such bond-rupturing effect was found selective at room temperature [10].

As demonstrated by various instrumental analyses, the [Bmim][Ac] did not destroy the special triple-helical structure of tropocollagen molecules that had been identified as being of importance for the functional and bioactive properties of collagen. According to these results, the discovery of [Bmim][Ac] as an ideal solvent for collagen may open up new possibilities for the chemistry and engineering of collagen, which has long been established as a readily accessible and renewable resource with many unique properties [10].

Preparation of amidoxime from nitriles in molecular solvent (usually in an alcohol) are accompanied by the amide side products. Surprisingly a selective formation of the desired amidoxime was observed in [Bmim][Ac] IL. No reaction occurred in imidazolium-based ionic liquids, containing other anions. The selectivity of the reaction was investigated for the preparation of a drug candidate's intermediate with similar result. Selective amidoxime formation in [Bmim][Ac] ionic liquid was proven for other model compounds too [11].

The internal redox esterification of α, β-unsaturated aldehydes and alcohols using different ionic liquids as catalysts and reaction solvents was carried out by [12] who found that the basic ionic liquid [Bmim][Ac] exhibited the best activity for this reaction.

Other applications of [Bmim][Ac] is in the biochemical industry where it can provide a strong addition to that industry as an ideal solvent for biomaterials involved in production processes, such as isolating lignin in paper pulp bleaching process, that provides an effective alternative to the conventional VOCs [13], Moreover, [Bmim][Ac] provides a useful extractor to separate collagen without destroying its intrinsic bioactive bonds when pure collagen is required as one of their ingredients.

3. Production of [Bmim][Ac]

There are several chemical paths to produce [Bmim][Ac], each of which can be considered as an alternative that requires certain design requirements mostly different from those required by the other alternatives. The anion exchange method can be used to produce water-soluble ionic liquids such as [Bmim][Ac] from reaction of halide ionic liquids such as [Bmim]Br, [Bmim]Cl, [Emim]Cl, etc. as a source of the anion and an acetate solution as a source of the acetate cation. The following is a summary of the several available paths for synthesis of [Bmim][Ac]:

1. An aqueous solution of 1-butyl-3-methylimidazolium bromide [Bmim]Br was allowed to pass through a column filled with anion exchange resin to obtain [Bmim][OH]. The aqueous [Bmim][OH] solution was then neutralized with equal molar acetic acid [CH_3COOH]. After removing water by evaporation under vacuum, the viscous liquid [Bmim][Ac] was thoroughly washed with diethyl ether, and finally dried under vacuum for 72 h at 70 °C [14].

2. Silver acetate (AgAc) (0.67 g, 4 mmol) was added to a solution of [Bmim]Cl (0.700 g, 4 mmol) in water (10 mL) and stirred at room temperature for 4 h. The suspension was filtered to remove silver chloride. The water was removed under vacuum to yield 0.69 g (85 wt.%) of a colorless oil [Bmim][Ac] [14].

3. Sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) was added to a solution of [Bmim]Cl (10 g, 57.25 mmol) in dry 2-butanone (500 mL). The reaction mixture was stirred vigorously for 12 h and afterwards filtered through Celite. An aqueous solution (500 mL) of acetic acid [CH_3COOH] (5.15 g, 85.87 mmol) was added then to the reaction mixture and stirred for half an hour. The organic phase was separated and washed with 50 mL of H_2O. The water was removed under vacuum to yield the product as a colorless liquid. The yield was 9.08 g (80 wt.%) [15].

4. [Bmim][Ac] can be synthesized by the addition of potassium acetate [CH_3COOK] to [Bmim]Cl IL in dry acetone. The formed KCl is insoluble and it precipitates and can be easily removed by filtration. But the main impurity in the [Bmim][Ac] product obtained by this method is the remaining [Bmim]Cl. In order to reduce this impurity, different amounts of [Bmim]Cl were added to [Bmim][Ac] and measured with an alkaline copper standard. Recovery rates of 90–98% [Bmim][Ac] was obtained over the whole range of the [Bmim]Cl concentration [16].

5. [Bmim][Ac] can be synthesized by dissolving [Bmim]Cl (0.25 mmol) in dry acetone (50 ml) and stirred with (5.0 g) ammonium acetate (CH_3COONH_4) at room temperature for 24 h to exchange the anion. The reaction mixture was then filtered off to remove precipitated ammonium chloride [NH_4Cl] and the excess ammonium acetate. The acetone was evaporated on rotary evaporator under reduced pressure and dried under vacuum to yield 96 wt.% [Bmim][Ac] [17].

6. [Bmim][Ac] can be synthesized by the addition of silver acetate [CH_3COOAg] (0.67 g, 4 mmol) to a solution of [Bmim]Cl (0.700 g, 4 mmol) in water (10 mL) and stirred at room temperature for 4 h. The suspension was filtered to remove the silver chloride precipitate by-product. The water was removed under vacuum to yield 0.69 g (85 wt.%) of a colorless [Bmim][Ac] IL [18].

The [Bmim][Ac] can also be synthesized by the slow addition of acetic acid [CH_3COOH] (10 mL, 180 mmol) to a 30 wt.% methanol solution of 1-Butyl-3-methylimidazolium methyl carbonate [Bmim][$MeCO_3$] (140 mL, 175 mmol) and stirred for 1 h under a dynamic vacuum (Schlenk line) to obtain [Bmim][Ac] (33.072 g; 167 mmol; 95% yield), which was further dried on a Schlenk line for 48 hours at 60 °C [16].

4. Alternatives processes for production of [Bmim][Ac]

In this work, we have qualitatively prioritized three different alternatives to provide a basis that helps in selecting the most suitable process alternative among the others to produce [Bmim][Ac] ionic liquid. These three process alternatives are discussed below.

Alternative 1: Butylation of 1-imidazole and methylation of 1-butylimidazole using Packed Bed Reactors (PBRs)

Here we have three main reactions as shown in the reaction schemes below: (1) Butylation of Imidazole by butyl iodide to produce Butylimidazole, (2) Methylation of the Butylimidazole by di-methyl carbonate to produce 1-Buty-3-methylimidazolium ion and acetate counter ion, (3) Ion-exchange reaction of the resulting

1-Buty-3-methylimidazolium ion and acetate counter ion to 1-butyl-3-methylimidazolium acetate [Bmim][Ac] in presence of excess acetic acid. See **Figure 1**.

Heating is required to bring the temperature of the first and second reactions to 150 °C and 210 °C, respectively. The third reaction is run at 80 °C. However, the second reaction must be operated at very high pressure (>70 bar), which is a special concern that requires very thick-wall equipment and further safety considerations. The reaction residence times for the first and the second reactions are 5 hr. and 2 hr., respectively. This alternative also uses Al_2O_3 catalyst to increase the reaction rate and decrease the residence time. However, using a catalyst increases the process cost; thus, it must be justified, especially if the reaction time is still high.

Alternative 2: Methylation of 1-butylimidazole using Packed Bed Reactors (PBRs)

Here we have two main reactions as shown in the reaction schemes below: (1) Methylation of Butylimidazole by dimethyl carbonate to produce 1-Buty-3-methylimidazolium ion and acetate counter ion, (2) Ion-exchange reaction of the resulting 1-Buty-3-methylimidazolium ion and acetate counter ion to 1-butyl-3-methylimidazolium acetate [Bmim][Ac] in presence of excess acetic acid. See **Figure 2**.

Heating is required to bring the temperature of the first and second reactions to 210 °C and 80 °C, respectively. However, the heating requirements here is less than that in Alternative 1. As in Alternative 1, high pressure (>70 bars), vacuum distillation, and use of Al_2O_3 catalyst, need to be considered in this alternative too. However, this alternative requires less time for the first reaction, which is, reduced from 5 to only 2 hours.

Alternative 3: Butylation of 1-methylimidazole using Micro-Structured Reactor (MSR)

Here we have two main reactions as shown in the reaction schemes below: (1) Butylation of Methylimidazole by 1-Chlorobutane to produce [Bmim]Cl. See for

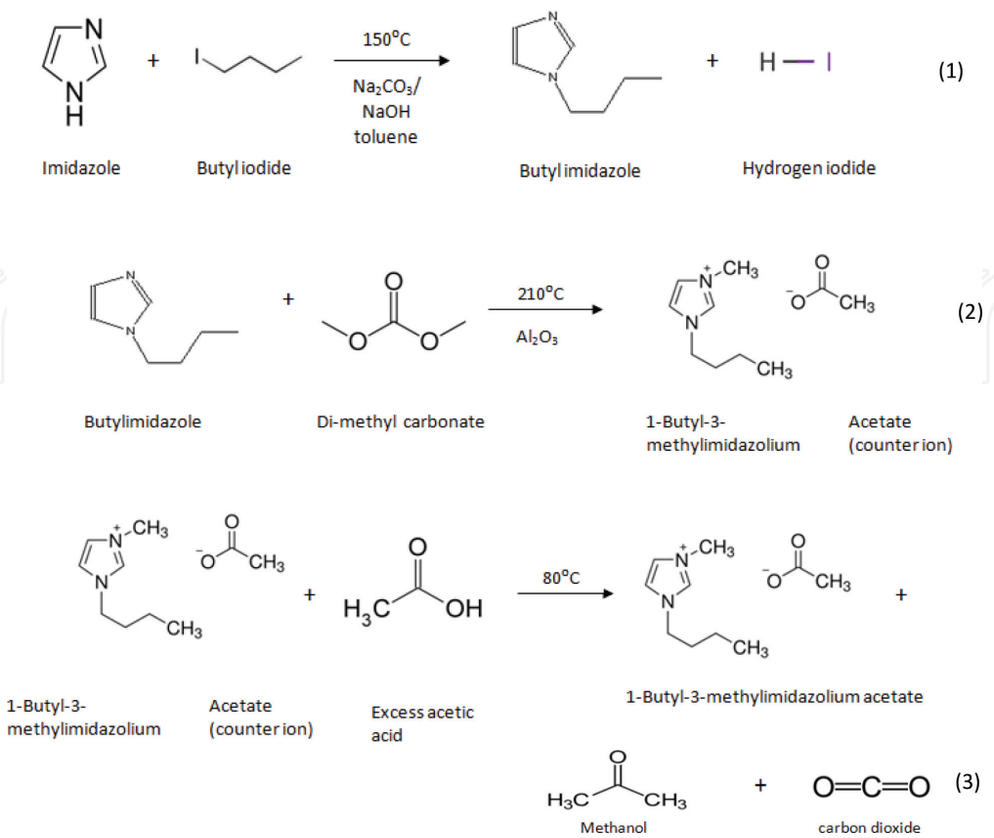


Figure 1.
Butylation of 1-imidazole and methylation of 1-butylimidazole using packed bed reactors (PBRs).

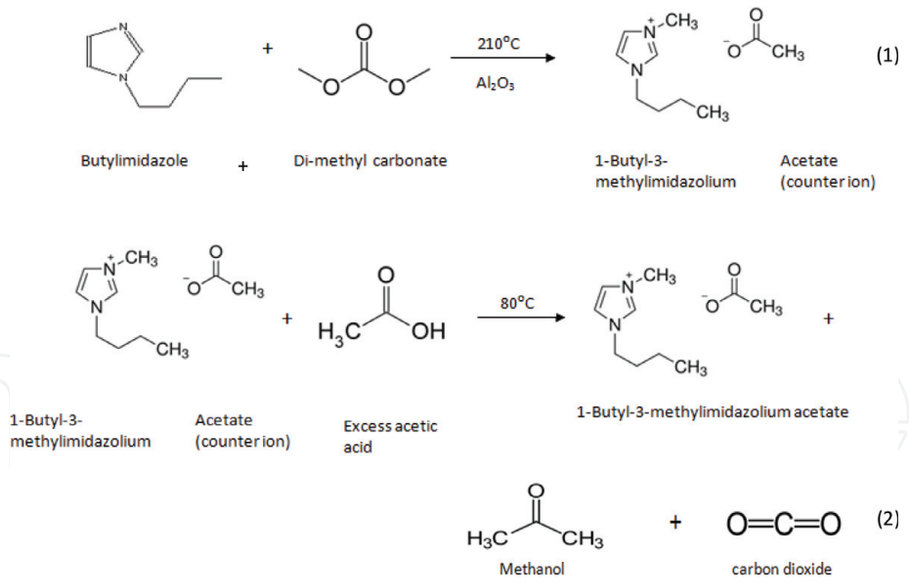


Figure 2.
Methylation of 1-butylimidazole using packed bed reactors (PBRs).

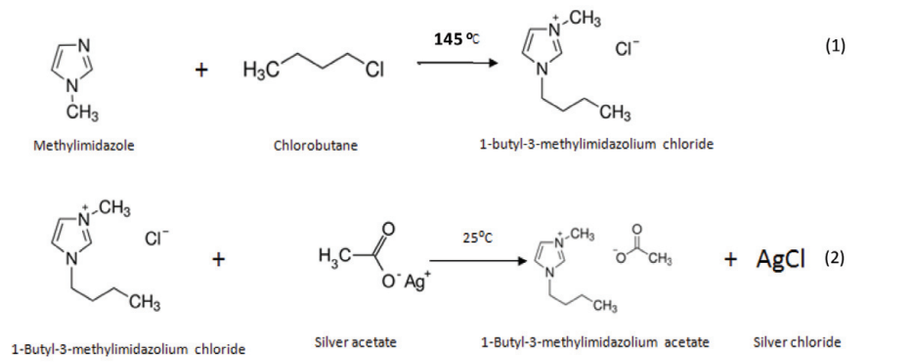


Figure 3.
Butylation of 1-methylimidazole using micro-structured reactor (MSR).

example, [14, 19, 20], (2) Ion-exchange reaction of the resulting [Bmim]Cl with silver acetate to produce 1-butyl-3-methylimidazolium acetate [Bmim][Ac] [21]. See **Figure 3**.

In this alternative, heating is only required in the first reaction to 145 °C where the pressure is around 6 bar. Also, the second reaction is operated at or near atmospheric pressure. This is a major advantage for this alternative where safety considerations and cost are dramatically reduced. The residence time for the first reaction is also relatively short (~32 min) at which about 87% conversion of the reactants is achieved when the reaction is carried out in a Micro-Structured Reactor (MSR) [22], which is definitely a great advantage for this alternative. The residence time for the second reaction is only few seconds if carried near room temperature. Another advantage of this alternative is that it does not require any catalyst in either reaction.

5. Comparison of [Bmim][Ac] production alternatives and process selection

In order to select the best process for commercial production of [Bmim][Ac] among the above three developed alternatives, a logical comparison procedure has been followed based on the following main criteria: Safety and environmental

criterion, preliminary economic feasibility criterion, operating conditions criterion, and process complexity criterion. Hence, a number of comparison tables were developed to give a clear picture about each of these alternatives and enable us in selecting the most promising alternative among the others.

Safety and environmental concerns criterion

Safety and protection of the environment are intrinsic considerations that should be focused on when designing a plant since for any success of the manufacturer, it is important that the personnel working in the industry and the environment surrounding it remains safe and complies with the nation's environmental regulations. In Alternative 1, high number of chemicals are involved in the process (see **Table 1**); most of which are flammable and combustible, i.e. might form explosive vapor mixtures and ignite near the source. Alternative 2 has almost the same number and type of chemicals (except imidazole) as in Alternative 1. Alternative 3 has only 4 chemicals; only two of which are flammable. Thus, Alternative 3 is considered to be the most environmentally-friendly and safe process among the studied three alternatives.

Preliminary economic feasibility criterion

Economic feasibility study is considered the first step in calculating and estimating the expected cost and profit for an industrial process. Hence, it enables the early evaluating for the cost and estimated profit for different alternatives. The preliminary economic feasibility is one important criterion used to evaluate the process production alternatives. It is a preliminary indication of the project's profitability, which is calculated by subtracting the cost of raw materials from the price of the final product [Bmim][Ac], according to the following definition:

$$\text{Preliminary economic feasibility} = \text{Price of [Bmim]Ac} - \sum \text{Costs of Reactants}$$

Chemical	Alternative	Safety and environmental concerns
Imidazole	1	May be combustible at high temperature [23]
Butyl iodide	1	Flammable liquid (Class 3). Vapors may form an explosive mixture with air [24]
Dimethyl carbonate	1 & 2	Highly flammable liquid; Flash point = 18 °C [25]
Acetic acid	1 & 2	Flammable in presence of open flames and sparks of heat. Ecotoxicity in water = 423 mg/L [26]
Hydrogen iodide	1	Non-flammable gas but hydrolyzes very rapidly yielding hydroiodic acid [27]
Methanol	1 & 2	Volatile and flammable. It may be slightly toxic to aquatic life
Toluene	1	Flammable
Butyl imidazole	2	Combustible: may burn but does not ignite readily. Flash point = 110 °C [28]
Methyl imidazole	3	Combustible [29]
1-Chlorobutane	3	Flammable liquid (Class 3). Low toxicity to aquatic organisms [30]
Silver acetate	3	Non-flammable. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment [31]
Silver chloride	3	Non-flammable. Does not pose adverse effect on aquatic life [32]

Table 1.
Safety and environmental concerns of the chemicals involved in the three alternatives.

Table 2 shows the individual chemicals prices in 2020 while **Table 3** shows the cost of reactants, the expected price for the sellable products and the difference between cost and sellable price for the desired product. **Table 2** also shows that Alternative 3 has the highest positive difference according to the above definition, and hence has the highest expected profit.

Process operating conditions criterion

Process operating conditions (pressure, temperature, reaction time, etc.) usually affect process selection, design and its economy since dealing with unfavorable conditions may raise safety concerns and increase process capital and operating costs (and thus process profitability). **Table 4** summarizes the process conditions for each of the studied alternatives. It is clear from **Table 4** that Alternative 3 can be

Compound	2020 Price (Euro, €)
1-Butyl-3-methylimidazolium acetate	980/kg
Imidazole	169/500 g
1-Butylimidazole	87.1/100 g
1-methylimidazole	141/500 g
Butyl iodide (1-Iodobutane)	125/500 g
Dimethyl carbonate	257/2 L
1-Chlorobutane	138/L
Aluminum oxide	137/kg
Acetic Acid	120/2.5 L
Methanol	73.7/L
Silver acetate	646/100 g
Silver chloride	5110/kg

Table 2.
Individual chemicals prices in 2020 [8].

Item	Alternative 1*	Alternative 2	Alternative 3
Reactants (and reagents)	Imidazole, Butyl iodide, Dimethyl carbonate, Al_2O_3 (catalyst), Acetic acid	Butyl imidazole, Dimethyl carbonate, Al_2O_3 (catalyst), Acetic acid	Methyl imidazole, 1-Chlorobutane, Silver acetate
Sellable Product(s)	[Bmim][Ac]	[Bmim][Ac]	[Bmim][Ac], AgCl
Cost of Reactants (Euro, €)	757.45	1061.07	2535.81
Price of Sellable Product (s) (Euro, €)	2765.00	2765.00	4933.38
Preliminary economic feasibility (Euro, €)	2007.55	1703.93	2397.57
Preliminary economic feasibility (US $)	2543.50	2158.80	3037.60

**The cost of NaOH, Na_2CO_3 and toluene are not counted in the preliminary economic feasibility.*

Table 3.
Preliminary economic feasibility results for the three alternatives studied in this work based on the raw materials' and final product(s)' prices.

Item	Alternative 1	Alternative 2	Alternative 3
Reactants	Imidazole, Butyl iodide, Dimethyl carbonate, Acetic acid	Butyl imidazole, Dimethyl carbonate, Acetic acid	Methyl imidazole, 1-Chlorobutane, Silver acetate
By-product(s)	CO_2, methanol, HI	CO_2, methanol	Silver chloride
Catalysts involved	Al_2O_3	Al_2O_3	None
Others	NaOH, Na_2CO_3, Toluene	None	None
Main reactions' temperatures (°C)	150, 210 and 80	210, 80 and 80	154 and room temperature
Main reaction pressure (bar)	70	70	6
Main reaction(s)' residence time	5 hr., 2 hr	7 hr	31.7 min, few seconds

Table 4.
Comparison of [Bmim][Ac] production alternatives in terms of reactants involved, products obtained, operating temperature, operating pressure, etc.

conducted at 145 °C and 6 bar for the first reaction and at near room temperature and 1 bar for the second reaction, which are much lower those required for Alternatives 1 and 2. Also Alternative 3 has the most favorable residence time (31.7 min for the first reaction and few seconds for the second reaction) when compared with those required for Alternatives 1 and 2. In addition, no catalyst is required for Alternative 3, while Al_2O_3 catalyst is required in the other two alternatives. So, one can say, Alternative 3 has the most favorable operating conditions among the three Alternatives studied.

Process complexity criterion

Since there are many compounds involved in Alternatives 1 and 2, the complexity of a process increases since more reaction and separation steps are needed and hence the capital and operating cost will dramatically increase. **Table 4** above shows Alternative 3 has the least number of compounds involved, thus it is the least complex alternative.

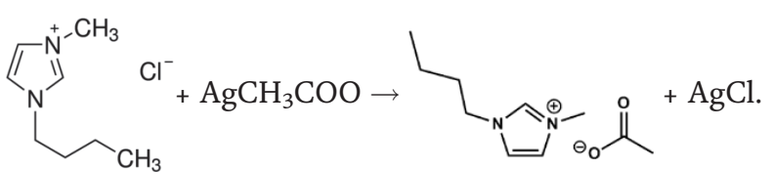
Thus, based on the analyses presented in **Tables 1–4** above, Alternative 3 has the highest preliminary feasibility and the most favorable operating conditions, the least process complexity and the minimum environmental and safety concerns.

6. Experimental setup, procedure and software used

Since most of the above methods are slow and require different solvents, the silver acetate [AgAc] method is used in this work to produce [Bmim][Ac] according to the following reaction:

$$[\text{Bmim}][\text{Cl}] + \text{AgAc} \rightarrow [\text{Bmim}][\text{Ac}] + \text{AgCl} \quad (1)$$

Or,



Or,

$$A + B \rightarrow C + D$$

Here, a silver chloride by-product is produced that can compensate for the cost of the silver acetate raw material. The experiment to produce the ionic liquid [Bmim][Ac] according to Eq. (1) was carried out in a CSTR.

The information available from literature [18] about this reaction are as follows: the conversion and reaction time at 25 °C are 84% and 4 h, respectively, when the ratio between [Bmim]Cl and silver acetate is 1:1.

As per the fact that ionic liquids are relatively newly researched species, their chemical analysis is of limited methods. Hence, from the reaction equation, one can notice that the only product that could be analyzed to follow up the progress of the reaction is AgCl. The Ag ions have some very common methods of determination such as titration or the most extensively used method gravimetric analysis. However, for the purpose of this experiment, sequential trials using the above-mentioned methods is time consuming and impractical considering the limited amount of precipitate. More about gravimetric analysis can be found elsewhere [33].

Noteworthy, the kinetics of the reaction could only be measured through the following up of the decrease in the concentration of Ag and/or Cl ions that could be easily monitored by the potentiometric detection technique based on ion-selective electrode. The potentiometric detection technique, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, application in colored and turbid solutions and low cost.

In this experimental work, a silver sheet coated with AgCl served as a working electrode and the reference electrode was a Jenway Ag/AgCl double junction containing 1.0 mol/L of lithium acetate solution in the outer compartment (shown in **Figure 4**). The cell potential was measured using a one-channel high-input impedance module (HIM) [34] attached to ADC-20 data acquisition card (purchased from Pico Technology Limited, London, UK) connected to a personal computer (PC). The potential was continuously output to the PC through the PicoLog recorder software. The electrochemical cell may be represented as follows: Ag/AgCl (s)/sample solution/1.0 mol/L CH_3COOLi salt bridge/4.0 mol/L KCl/Ag/AgCl.

In this work, a newer, more sophisticated method of monitoring Ag ion concentration was chosen which is known as data acquisition method. The system control is maintained through a data logging software which uses electrodes to detect the potential difference of the solution with time. This method was chosen here because

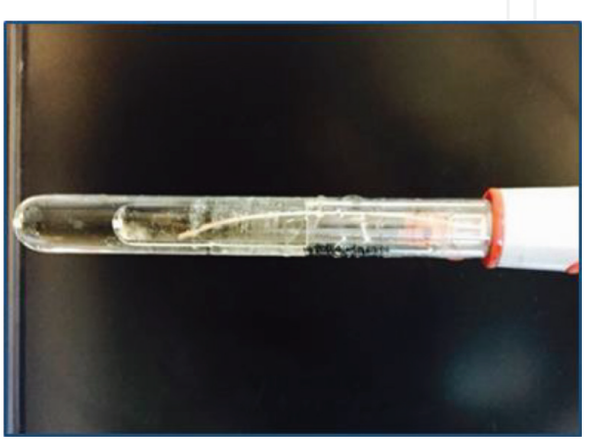


Figure 4.
Jenway Ag/AgCl double junction reference electrode.

it is fast and produce accurate results, it requires minimal monitoring and it is reliable to be used for a large number of runs. The few limitations associated with this method is the need for calibration for each run to get the unique relationship between the potential difference and concentration.

The main instrument used for the data acquisition was the Picolog® high-resolution data logger from Pico Technology [35]. It allows the experimenter to achieve fast and reliable results due to its ability to detect small changes. Also, ease of manipulating and displaying of data makes this particular setup a useful component to have numerous readings at a predetermined sampling rate. It is also powered directly by the PC connection and does not require external batteries or power source [35].

7. Generation of Ag^+ concentration calibration curves

Since the analytical technique to measure the Ag ion concentration does not measure the concentration directly, a calibration curve and subsequently a calibration equation is required to form the relationship between the signal, which is the potential in millivolts (mV), and the molar concentration (M). The complete setup is shown in **Figure 5**.

The experimental procedure used in this work is as follows:

1. To a 100 mL double walled beaker, add 50 mL of water and 5 mL of potassium acetate (x M) for the purpose of adjusting the ionic strength and obtaining a steady baseline.

2. Fill the circulating water bath with ice water to keep a low temperature since a test run of the experiment at room temperature indicated that the reaction was very fast and therefore to better study the reaction kinetics, a temperature < 25 °C was used.

3. Prepare three standard solutions of silver acetate (AgAc) with molar concentrations of 0.0001 M, 0.001 M and 0.01 M.

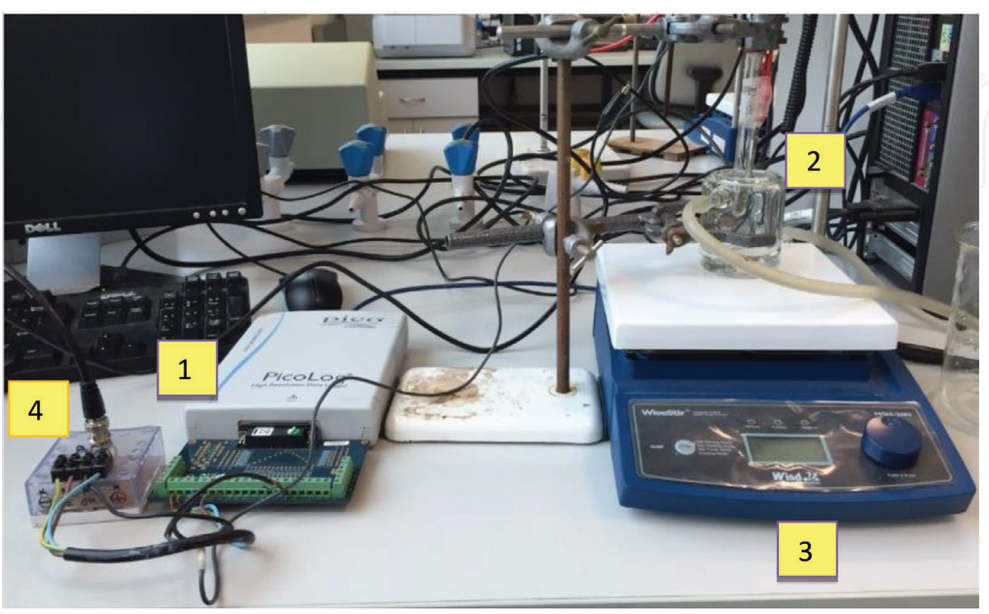


Figure 5.
Experimental setup; 1: PicoLog data logging device, 2: Glass beaker, 3: Stirring plate, 4: High-input impedance module (HIM).

4. Sequentially add appropriate small aliquots of AgAc standards and record the potential (mV) continuously. A final Ag ion concentration range of ($2.37x10^{-6}$ – $5.14x10^{-4}$ M) was tested to check the Nernstian response of the working electrode in order to select a reasonable initial AgAc concentration in the subsequent reaction kinetics tests.

5. Generated the graph of the potential signal (mV) vs. the AgAc molar concentration (M).

For Run #1 (at T = 12 °C), the calibration curve data are shown in **Table 5** and **Figure 6**, and the plot of the calibration curve is shown in **Figure 7**. The experiment was run at the same temperature at which the calibration was performed, and therefore for any subsequent runs at different temperatures, a different calibration curve is required.

AgAc concentration (M)	2.37E-06	4.72E-06	2.82E-05	5.14E-05	2.84E-04	5.14E-04
Potential (mV)	240.6	248.6	255.3	258.4	299.2	337.1

Table 5.
Calibration curve data at T = 12 °C.

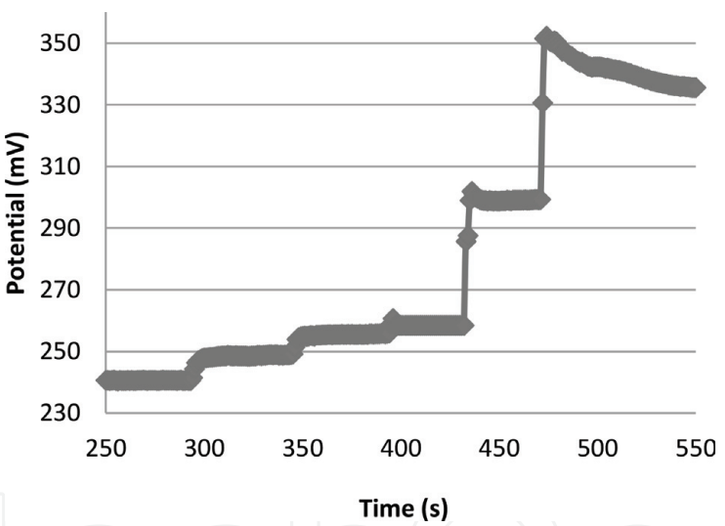


Figure 6.
The trend of the potential difference versus time for run #1 at T = 12 °C).

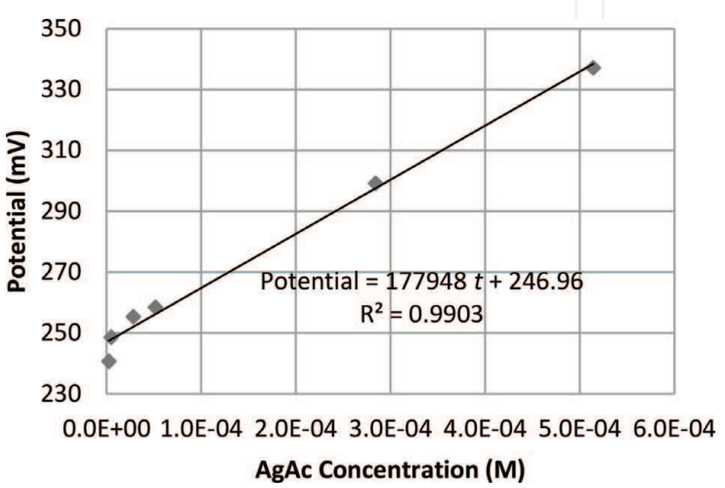


Figure 7.
Calibration-curve linear fit of the potential (mV) vs. AgAc molar concentration (M) for run #1 (at 12 °C).

8. Experimental results and analyses

The main objective of this experiment is to determine the kinetic data necessary to design a continuous stirred tank reactor (CSTR) for the production of 1-butyl-3-methylimidazolium acetate [Bmim][Ac] from the reaction of 1-butyl-3-methylimidazolium chloride [Bmim]Cl and silver acetate (AgAc), i.e. to determine the rate equation of the reaction and its order with respect to both reactants, the reaction rate constant (k) as a function of temperature, and the reaction activation energy (E_a). Several experimental runs for the reaction presented by Eq. (1) have been carried out. The purpose of each of these tests is also outlined below.

Run #1: Excess reactant method (isolating [Bmim]Cl) for the determination of the partial orders of the reactants.

A pseudo-first order reaction is a reaction where one of the reactants is present in large excess compared to the other reactant such that its concentration does not change significantly with time. In this case, the concentration of the excess reactant, say A, can be assumed to be constant and is absorbed into the rate constant k to give a pseudo-first order rate constant $k' = k\,C_A$. So, for the reaction presented by Eq. (1), $C_A >> C_B$, then $\Delta C_A \approx 0$ [36].

In the same way, some second and higher-order reactions can be more easily examined when the concentration of one reactant is essentially held constant (by using a large excess of that reactant) such that the fractional change in its concentration over the course of reaction is negligible [37].

Here Run #1 was carried out at 12 °C using excess of reactant A (i.e. [Bmim]Cl). The rate equation for the reaction presented by Eq. (1), is given by

$$-r_A = -\frac{dC_A}{dt} = (k\,{C_A}^{\alpha})\,{C_B}^{\beta} = k'{C_B}^{\beta} \tag{2}$$

where k is the reaction rate constant and k' is the reaction rate constant in presence of excess A (i.e. [Bmim]Cl). Here B stands for the silver acetate [AgAc]. Since

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k'{C_B}^{\beta} \tag{3}$$

By integration of Eq. (3), we get

$$\ln\left(-\frac{dC_B}{dt}\right) = \ln k' + \beta \ln C_B \tag{4}$$

The potential vs. time and reactant B (i.e. AgAc) concentration vs. time are shown in **Figures 8** and **9**, respectively. Both curves are straight lines with $R^2 \approx 1.0$.

From **Figure 9**, the AgAc concentration, $C_B = -0.000459\,t + 0.0001867$, thus $-\frac{dC_B}{dt} = -0.000459$, or $\frac{dC_B}{dt} = 0.000459$, i.e. it is constant. Thus, the plot of $\ln\left(-\frac{dC_B}{dt}\right)$ versus $\ln C_B$ will be a horizontal line with a zero slope. Accordingly, $\beta = 0$ and the reaction rate is of zero order with respect to the AgAc concentration.

Run # 2: Using the equimolar method for the determination of the partial orders of the reactants.

In order to determine the overall order of a chemical reaction, it is more convenient to use equimolar concentrations of the reactants A and B at the start of the reaction (i.e. $t = 0$) [38]. So, for the reaction presented by Eq. (1), and at any time t, the [Bmim]Cl concentration is equal to the AgAc concentration, or $C_A = C_B = C_0 - x = C$, where x is the reacted mole fraction of either component.

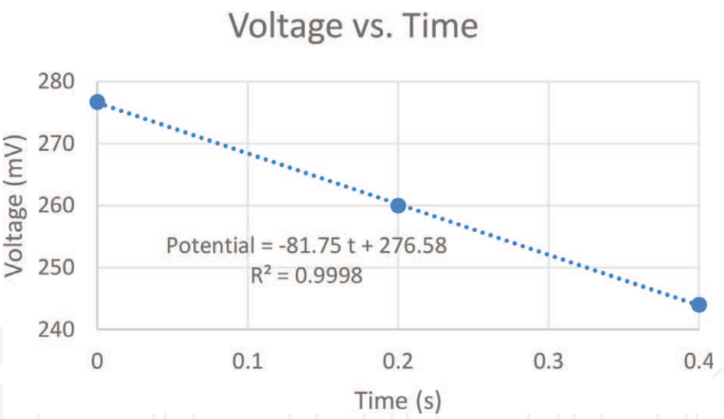


Figure 8.
Potential (mV) vs. time curve for run #1 at T = 12 °C.

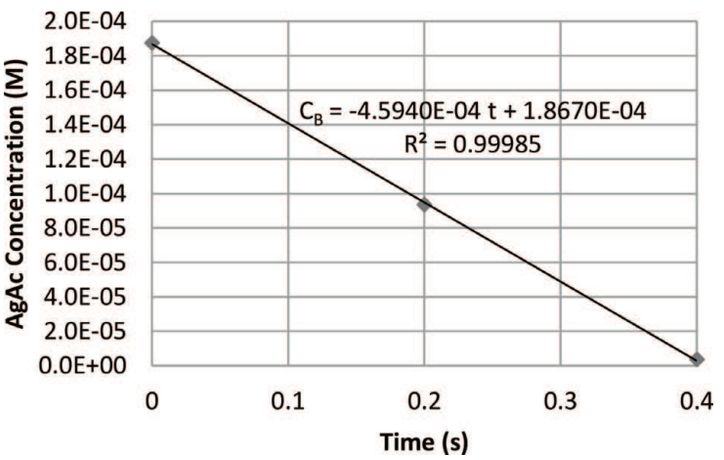


Figure 9.
AgAc concentration vs. time for run #1 at T = 12 °C.

In this case, Run # 2 was carried out at 12 °C using equimolar amounts of [Bmim]Cl and AgAc. The rate equation in this case can be rewritten as:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k\,C_A{}^{\alpha+\beta} \tag{5}$$

where β was found to be zero (earlier in Run #1 results) when [Bmim]Cl was used in excess. Here we have two options for the C_A exponent (either α = 1 or $\alpha \neq 1$).

For α = 1, Eq. (5) can be rearranged to give

$$-\frac{dC_A}{C_A} = k\,dt \tag{6}$$

By integration of Eq. (6), we get:

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k dt \tag{7}$$

Or,

$$\ln\left(\frac{C_A}{C_{Ao}}\right) = -k\,t \tag{8}$$

Or,

$$C_A = C_{Ao}\, e^{-kt} \tag{9}$$

The AgAc molar concentration (M) and the corresponding ln (C_{Ao}/C_A) vs. time for Runs #2 are given in **Table 6**. The plot of ln (C_{Ao}/C_A) vs. time is shown in **Figure 10**; from which $C_A = C_{Ao}\, e^{-kt} = C_{Ao}\, e^{-0.02079\, t}$. Here, $R^2 = 0.9425$, which means that the ln (C_{Ao}/C_A) vs. time is almost linear ($\alpha \approx 1.0$) and a first-order [Bmim]Cl concentration is a valid assumption.

For $\alpha \neq 1$, Eq. (7) becomes

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A^{\alpha}} = \int_0^t k dt \tag{10}$$

and the solution of Eq. (10) can be written as

$$\frac{C^{1-\alpha} - C_0^{1-\alpha}}{\alpha - 1} = k\, t \tag{11}$$

However, several attempts have been made in this work to find the non-integer value of α based on Eq. (11). In all runs and at all tested temperatures, the value of α was ≈ 1.0, which means that the first-order [Bmim]Cl concentration is still a valid assumption.

Now, in order to determine the *k* value as a function of temperature, two more runs have been conducted at 37.6 **°C** and 50 **°C**. The results are displayed below.

Time (s)	AgAc concentration (M)	Potential (mV)	ln (C_{Ao}/C_A)
0	0.0000818	257.919	0.0
1	0.0000794	257.486	0.02978
2	0.0000778	257.199	0.05014
3	0.0000769	257.042	0.06177
4	0.0000758	256.848	0.07618

Table 6.
AgAc molar concentration (M) and ln (C_{Ao}/C_A) vs. time for runs #2 at 12 °C.

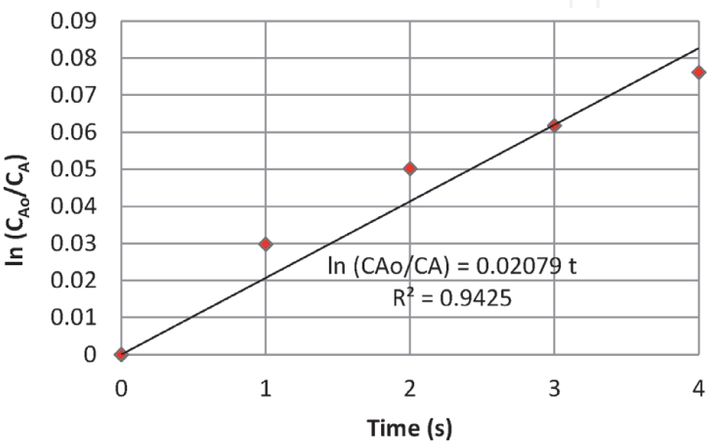


Figure 10.
Ln (C_{Ao}/C_A) vs. time for run #2 at 12 °C. ◆: Exp, ___: linear fit.

Run #3: Reaction kinetics at T = 37.6 °C.

This run was carried out using equimolar concentrations of the reactants A and B at the start of the reaction. The calibration curve data for this run are given in **Table 7**. The corresponding plots of the potential (mV) vs. AgAc molar concentration (M) and ln (C_{Ao}/C_A) vs. time are shown in **Figures 11** and **12**, respectively. Here, R^2 = 0.9443, and the ln (C_{Ao}/C_A) vs. time is almost linear ($\alpha \approx 1.0$) and is first order with respect to the [Bmim]Cl concentration. As seen from **Figure 12**, the rate constant at 37.6 °C is 0.50865 s^{-1}.

Run #4: Reaction kinetics at 50 °C.

Again, this run was carried out using equimolar concentrations of the reactants A and B at the start of the reaction. The calibration curve data for this run are given in **Table 8**. The corresponding plots of the potential (mV) vs. AgAc concentration (M) and ln (C_{Ao}/C_A) vs. time are shown in **Figures 13** and **14**, respectively. Again, R^2 = 0.9671 ≈ 1.0, and the ln (C_{Ao}/C_A) vs. time is almost linear ($\alpha \approx 1.0$) and first order with respect to the [Bmim]Cl concentration. As seen from **Figure 14**, the rate constant at 50 °C is 0.92047 s^{-1}.

From the linear fits of ln (C_{A0}/C_A) vs. time at the test temperatures 12, 37.6 and 50 °C, **Table 9** shows the rate constant (k) values vs. temperature.

Lastly, **Figure 15** shows the linear fit plot of ln k vs. 1/T. That is

$$\ln\,(k) = \ln(k_o) - \left(\frac{E_a}{R}\right)\frac{1}{T} \tag{12}$$

Time (s)	AgAc concentration (M)	Potential (mV)	ln (C_{Ao}/C_A)
0	0.000283	321.8	0.0
1	0.000239	314.6	0.17030
2	0.000105	292.9	0.99030
3	0.000417	282.6	1.91423
4	0.000374	281.9	2.02320
5	0.000257	280.0	2.39790

Table 7.
Calibration curve data for run #3 at T = *37.6 °C.*

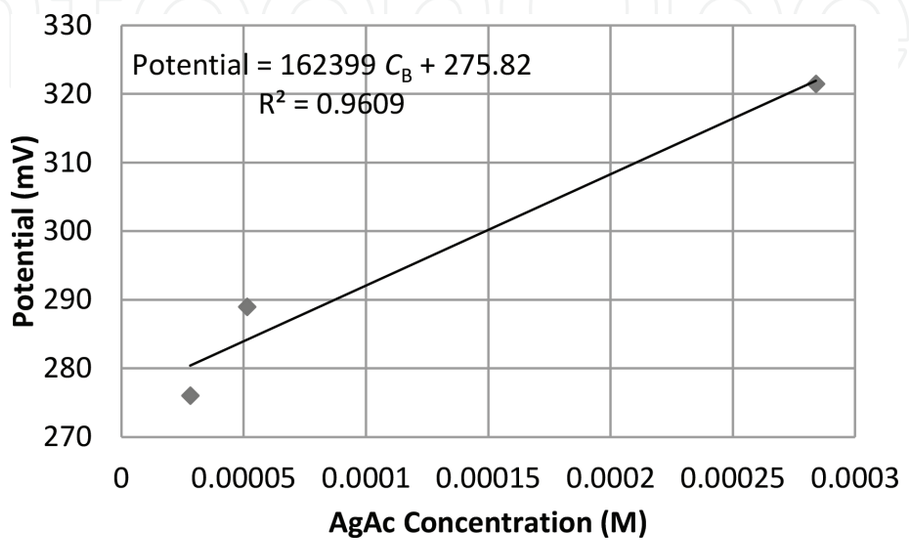


Figure 11.
Calibration-curve for potential (mV) vs. AgAc molar concentration (M) for run #3 at 37.6 °C.

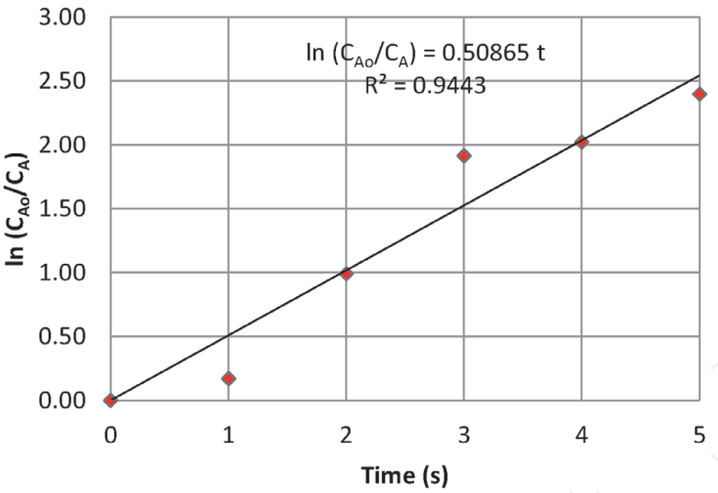


Figure 12.
Ln (C_{Ao}/C_A) vs. time for run #3 (at T = 37.6 °C); ♦: Exp, ___: linear fit.

Time (s)	AgAc concentration (M)	Potential (mV)	ln (C_{Ao}/C_A)
0	2.27E-04	299	0
0.2	1.97E-04	295.5	0.14085
0.4	1.72E-04	292.5	0.27971
0.6	1.42E-04	289	0.4706
0.8	1.08E-04	285	0.74555
1	8.31E-05	282.1	1.00617

Table 8.
Calibration curve data for run #4 at T = 50 °C.

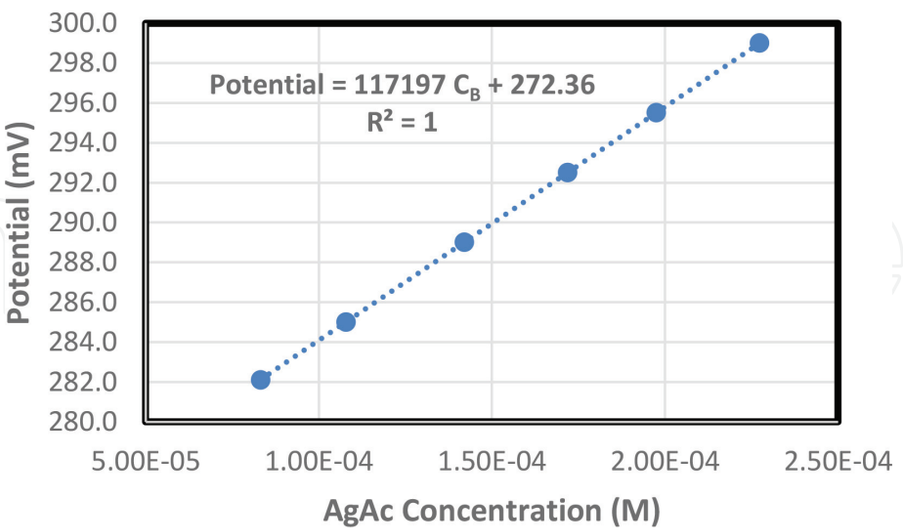


Figure 13.
Calibration-curve for potential vs. AgAc molar concentration for run #4 at 50 °C.

Figure 15 indicates that the relationship between ln k and $1/T$ is almost linear with R^2 = 0.9776. However, using the fitting parameters shown on **Figure 15**, the Arrhenius constant k_o and the activation energy E_a are determined as follows:

$$k_o = e^{29.668} = 7.67 \times 10^{12} \text{ L/mol.s.}$$

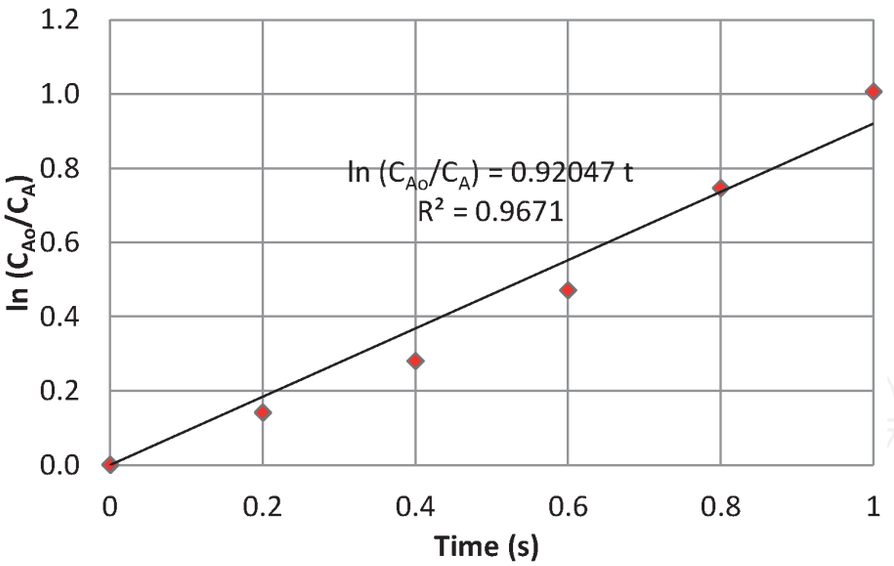


Figure 14.
Ln (C_{Ao}/C_A) vs. time for run #4 (at T = 50 °C*);* ◆*: Exp,* ___*: Linear fit.*

T (°C)	12	37.6	50
T (K)	285.15	310.75	323.15
k (s^{-1})	0.02079	0.50865	0.92047

Table 9.
Rate constant k *vs.* T *for the [Bmim][Ac] production reaction presented by Eq. (1).*

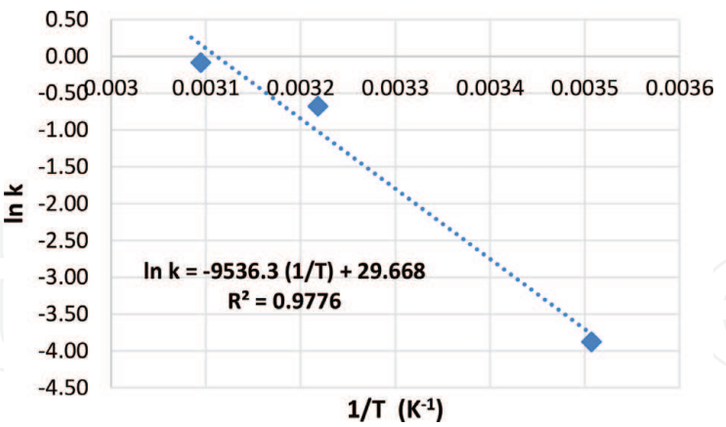


Figure 15.
Plot of ln k *vs. 1/*T *for [Bmim][Ac] production for the reaction presented in Eq. (1).*

$$E_a = 8.314 \times 9536.3/1000 = 79.285 \text{ kJ/mol.}$$

Finally, Eq. (12) can be written as.

$$k = k_o\, e^{(-Ea/RT)} = 7.67\text{x}10^{12}\, e^{(-79.285/RT)} \tag{13}$$

Here, the Arrhenius constant k_o is extremely high, which means that the reaction of [Bmim]Cl and silver acetate to produce [Bmim][Ac] and silver chloride is extremely fast.

9. Conclusion

In this work, the kinetic data for the reaction of [Bmim]Cl and silver acetate to produce [Bmim][Ac] and silver chloride, were experimentally determined. The order of the reaction was found to be of first order with respect to [Bmim]Cl and of zero order with respect to silver acetate. The rate constant as a function of temperature was found to be $k = 7.67\text{x}10^{12}\ e^{(-79.285/RT)}$. That is, the values of k_o and E_a are $7.67\text{x}10^{12}$ L/mol.s and 79.285 kJ/mol, respectively. This indicates that the [Bmim]Cl reaction with silver acetate to produce [Bmim][Ac] and silver chloride is extremely fast. It should be mentioned here that the produced silver chloride has a very high-market value that can easily compensate for the high-initial cost of the silver acetate reactant.

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