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EUTECTIC BASED IONIC LIQUIDS BETAINE-LEVULINIC ACID: SYNTHESIS, PHYSICOCHEMICAL PROPERTIES AND TECHNOECONOMIC ANALYSIS AS LIXIVIANT TOWARDS RED MUD

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Abstract

This study aims to develop Eutectic Ionic Liquids (EILs) as an environmentally friendly solvent that can be used in various applications, especially in the industrial field. EILs were synthesized through Solv metallurgical method by mixing betaine (Hydrogen Bond Acceptor, HBA) with levulinic acid organic compound (Hydrogen Bond Donor, HBD) with molar ratio of 1:3, 1:4, 1:5, 1:6, and 1:7. The composition of the synthesized EILs was characterized using FTIR, their thermal behaviour was analysed using Differential Scanning Calorimeter (DSC) and physiochemistry using Cyclic Voltammetry (CV). The optimal composition of betaine-levulinic acid EILs based on DSC data showed an exothermic reaction that produced the lowest freezing point of -32°C at a ratio of 1:7, Thermogravimetric Analysis-Differential Thermal Analyzer (TGA-DTA) analysis results of EILs thermal stability is between the two initial components. FTIR results showed that the characteristic peaks in the spectra of betaine, levulinic acid, and betaine-levulinic acid EILs were caused by the formation of hydrogen bonds between hydroxyl groups. Physicochemical properties test (electrochemical window) using CV technique showed good electrochemical stability results. The synthesized betaine-levulinic acid EILs were analysed for techno-economic evaluation as a lixiviant for red mud recovery, which resulted in a positive return and is an environmentally friendly material.

Keywords: Betaine, Levulinic acid, Eutectic ionic liquids (EILs), Eco-friendly, Evaluation techno-economy.

1. Introduction

Since the last two decades, only a small number of research experts have recognized the term Ionic Liquids (ILs). They tried to research that ILs can be the best reaction solvents for various types of reactions, such as alkylation, acid hydrolysis, Beckmann rearrangement, carbonization, esterification, depolymerization, polymerization, and pre-extraction, etc. [1]. ILs are also considered to be good molecular solvents and/or environmentally friendly, and currently ILs have received great attention in various fields such as catalysis, electrochemistry, materials chemistry, and biomass pre-treatment [2].

ILs are molten salts composed entirely of cations and anions and are often described as liquids under certain temperatures, such as 100 °C or room temperature, but keep in mind that these temperatures cannot be used as a benchmark for a substance to be considered an IL. Other salts, such as sodium chloride, differ from ILs in that their solid structure and strong ionic interactions make them liquid at very high temperatures (>800°C) [3]. The large and unsymmetrical structure of the constituent ions leads to a lower melting point of ILs. The ions can be combined in various combinations to change their thermophysical properties [4]. However, conventional ILs have several disadvantages, including high volatility, flammability, and reaction instability [5]. These characteristics are not promising for wider application.

There are various types of ILs based on their constituent components, including Poly ionic liquids (PILs), polyelectrolytes that can be obtained from the polymerization of ionic liquid monomers or through post-polymerization processes [6], PILs combine the advantages of ILs and polymers, and have the ability to modify their intrinsic physicochemical properties in a superior manner, and are recyclable [7].

However, the synthesis process of PILs is complicated [6]. Functionalized Ionic Liquids (FILs) have also been developed as an innovation to overcome the drawbacks of PILs. FILs are the incorporation of functional groups from their cations and/or anions, which can act as organic phases and extraction agents in metal recovery processes, and Rare Earth Elements (REEs) [8] FILs have good performance in extractant mixing, facilitating solvent recovery, and overcoming the environmental impact of REEs separation [9].

However, the hydrometallurgy method in the synthesis of FILs is considered less practical [8]. Therefore, alternative formulations and methods for the synthesis of FILs are needed, among others, through the development of eutectic ionic liquids (EILs).

EILs can be synthesized using the eutectic mixing technique, which is the mixing of two substances that act as hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). The freezing point of these two substances is much lower than the freezing point of each substance [10]. EILs are dipolar, non-flammable, and thermal stability which are characteristics of new solvents produced by the interaction between the two elements. In an effort to reduce or eliminate conventional solvents, as well as alternative sustainable environmentally friendly materials [11]. EILs have the advantages of high biocompatibility and biodegradability, easy synthesis process, low cost, and high availability of raw materials, so EILs will be widely used in various fields [12].

In previous research, EILs from choline chloride and several carboxylic acids were analysed and used as catalysts for the conversion of levulinic acid to ethyl levulinate with the addition of ethanol [13]. However, the use of ethanol results in high volatility. Then, based on research that has also been done in the manufacture of seven types of EILs using betaine as HBA with various variations of HBD ratios, namely betaine + DL-lactic acid (1:2), betaine + DL-lactic acid (1: 5), betaine + DL-lactic acid + water (1:1:1), betaine + levulinic acid (1:2), betaine + citric acid + water (2:1:6), L-proline + levulinic acid (1:2) and L-proline + DL-lactic acid (1:1) resulted in high viscosity [14], but in that study the optimum composition was not known and the process used hydrometallurgy.

On the basis of these studies, the objective of this research is to develop environmentally friendly EILs, synthesized through a Solv metallurgy approach using variations in the betaine-levulinic acid molar ratio to produce a good and sustainable solvent composition, and analysed techno-economically. A techno-economic evaluation will provide an estimate of all costs and revenues associated with a large industrial process project. To determine the economic prospects of a project, an economic evaluation was conducted to test the feasibility of lixiviant to recovery red mud using betaine-levulinic acid EILs.

2. Method

The materials used in this study were betaine (Sigma-Aldrich, perchloric acid titration ≥98%, solid, MW: 117.15 g/mol) and levulinic acid (Sigma-Aldrich, technical grade 90%, liquid, MW: 116.11 g/mol).

2.1. Synthesis of eutectic ionic liquids

The synthesis of EILs was carried out by mixing the two components of betaine as HBA and levulinic acid as HBD in a Schlenk tube, mixing betaine with levulinic acid was carried out by varying the ratio of 1:3 to 1:7 with a molarity of 0.03 mol, then the heating process using a sand bath on the surface of a hot plate with a temperature of about 80-100°C, stirred using a 500rpm magnet until a homogeneous solution was formed.

2.2. Characterization

Characterization of betaine-levulinic acid EILs using Fourier-Transform Infrared Spectroscopy (FTIR) instrument (Prestige 21 Shimadzu FTIR Spectrometer) recorded spectra at 400-4000 cm-1 resolution of 1 cm-1 which aims to identify functional groups and analyse the mixture in EILs. Next, thermal tests of betaine-levulinic acid EILs were carried out using a Differential scanning calorimetry (DSC) instrument (NETZSCH DSC 214 Polyma) in the temperature range of 25°C-(-)150°C, nitrogen atmosphere (50 mL/min), with a concentration of 5-10 mg of sample aimed at determining the thermal properties of EILs and the optimal molar ratio in the presence of eutectic points.

Analysed by Differential Thermal Analysis and Thermogravimetric Analysis (TG-DTA, 7-Perkin Elmer) at 25-600°C at a rate of 10°C operating in dynamic and isothermal modes under nitrogen atmosphere to perform thermogravimetric analysis. The physicochemical properties (electrochemical window) were then tested using Cyclic Voltammetry (CV, metrohm 797 VA Computerise Voltammeter, Carbon working electrode, Ag/AgCl comparison electrode and Pt auxiliary electrode) technique to determine the electrochemical stability with a potential range of -0.9 V to 0.9 V.

2.3. Evaluation techno-economical

The techno-economic analysis in this study consists of engineering evaluation and economic evaluation. First, the engineering evaluation was conducted to test the technical feasibility of the process. The mass balance calculation supported this evaluation for designing industrial processes on a large scale. The design was based on the following assumptions.

- All reactants were completely consumed.
- The reaction conversion rate was assumed to be 100% without any by-product.
- The final product is the synthesized EILs Betaine-levulinic acid obtained for large-scale calculation with the value of the economic evaluation parameters produced under ideal conditions is positive.

3. Results and Discussion

3.1. Synthesis of EILs betaine-levulinic acid

Eutectic Ionic Liquids (EILs) have been successfully synthesized by mixing betaine and levulinic acid organic compounds in a molar ratio of 1:3 to 1:7. In this study, betaine was used as HBA, because betaine is a zwitterion, i.e., it has both positive and negative formal charges, so the carboxylic group of betaines itself is a strong hydrogen bond acceptor [15], While the EILs constituent that acts as an HBD in this study is levulinic acid, as it is highly effective as a leaching agent (both pure and as part of DES), and can be produced from a variety of renewable sources, such as sugar industry by-products (cellulose), starch-loaded waste, and other sources [16].

The optimum molar ratio of betaine-levulinic acid in the synthesis of EILs was determined based on the eutectic characteristics of EILs from DSC measurements. Figure 1 shows the physical properties of EILs synthesized from betaine and levulinic acid.

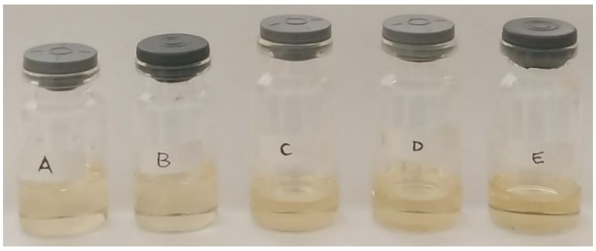

Fig. 1. EILs photograms of synthesized betaine-levulinic acid with molar ratios of 1:3 (A), 1:4 (B), 1:5 (C), 1:6 (D), and 1:7 (E).

Based on Fig. 1, it can be stated that the synthesized EILs at a ratio of 1:3 to 1:7 show a thick, homogeneous, and unscented solution. These findings indicate the success of EILs synthesis in the molar ratio range. Next, the synthesized EILs were characterized using FTIR, DSC thermal properties test, TGA-DTA and CV analysis to test their physicochemical properties, and then the techno-economic evaluation as a lixiviant for red mud will be analysed.

3.2. Thermal test of EILs using DSC

In this study, DSC was used to determine the temperature range of the liquid crystal phase of the synthesized betaine-levulinic acid EILs. Melting temperature indicates the temperature at which the crystalline solid phase changes to an ionic liquid crystal phase, and freezing indicates the temperature at which the ionic liquid crystal phase changes to an isotropic liquid (freezing) phase. Figure 2 shows the DSC thermogram of the EILs compound betaine-levulinic acid.

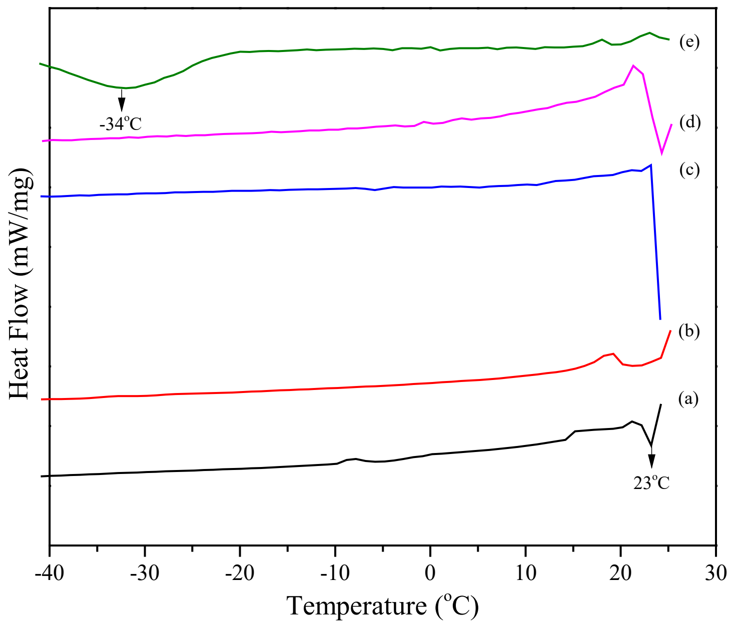

Fig. 2. DSC thermograms of EILs betaine-levulinic acid molar ratios 1:3 (a), 1:4 (b), 1:5 (c), 1:6 (d), and 1:7 (e).

Figure 2 shows the temperatures and enthalpies of freezing, crystallization and glass transition of betaine, levulinic acid and EILs at various molar ratios indicating the reaction of EILs formation is exothermic. The freezing process indicated by the peak of the curve indicates the cold crystallization process, where amorphous crystals transform through melting process into crystalline ones. In the betaine-levulinic acid EILs with a molar ratio of 1:3-1:7, shows a decrease in temperature that illustrates the typical dissolution pattern in EILs. This relationship is seen through changes in area and peaks, which correspond to an increase in ionic disorder in the solid phase prior to the melting process [17].

The eutectic properties of EILs precursors can be measured by mixing two materials in a certain molar ratio with a lower melting point, which indicates the success of EILs synthesis [10]. The mixed phase of EILs is characterized by the lower melting point or high freezing point of its constituent components, as shown in Fig. 3. The pure betaine and pure levulinic acid components have freezing points of 14°C and -32°C, respectively. However, once betaine and levulinic acid are mixed to form EILs, a significant temperature drop occurs, which causes the liquid phase to become a solid phase [18].

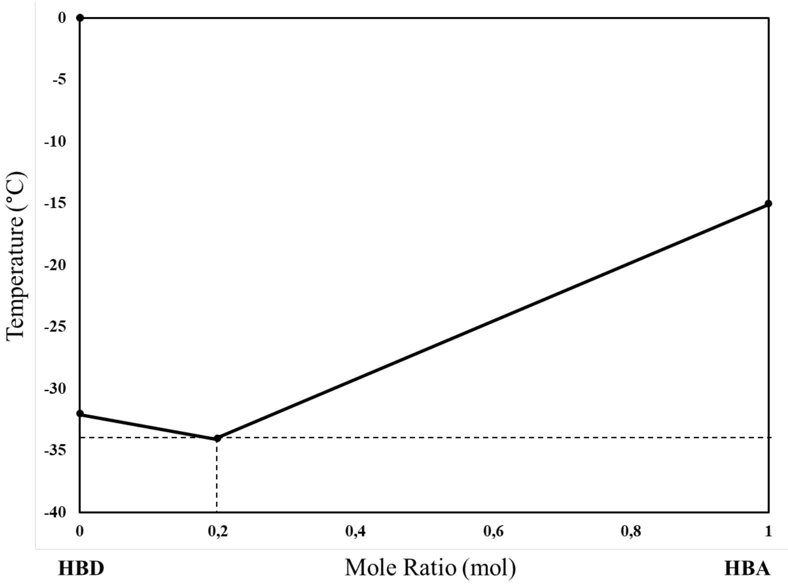

Fig. 3. Temperature eutectic phase diagram of betaine-levulinic acid EILs composition at 1:7 molar ratio.

The process of interaction of betaine cation molecules with levulinic acid anions through hydrogen bonding leads to an increase in the crystalline freezing temperature. As a result, the hydrogen bonding interaction between the cation and the chloride anion is reduced, resulting in a decrease in the melting point and an increase in the freezing point of EILs [19].

Obtaining the right composition can facilitate better thermal stability of the individual components, making it easier for the final product purification process. In this study, the lowest freezing point was obtained at a molar ratio of 1:7, having the lowest freezing point in liquid form at room temperature and a more homogeneous mixture so that at a molar ratio of 1:7 which can form a eutectic point [20], while at a molar ratio of 1:3 to 1:6 the resulting freezing point is less than optimal due to low detection of tools and it is possible that other factors affect it so that it cannot form the eutectic diagram equation.

3.3. Analysis of EILs using TGA-DTA

Thermal analysis for the melting point of betaine-levulinic acid EILs was carried out using TGA-DTA as a precursor, as shown in Fig. 4. From Fig. 4, an endothermic process occurs, where the glass transition occurs at Tg at temperatures around 306°C to 172°C. There is a small change in heat capacity on cooling, the presence of Tg at temperatures much lower than the melting point of the pure component confirms the formation of EILs [14].

Figure 4 shows the TGA and DTA thermograms of EILs of betaine-levulinic acid with a molar ratio of 1:7. In the TG curves of temperatures between 172 and 250°C, the decomposition of betaine and levulinic acid caused a mass loss of about 2.1% and the decomposition at 250°C which is the initial degradation temperature (ton set) and 306°C is the final degradation temperature (tend set) of the betaine-levulinate acid EILs which lost about 12.3% mass indicating the maximum working temperature of this solvent.

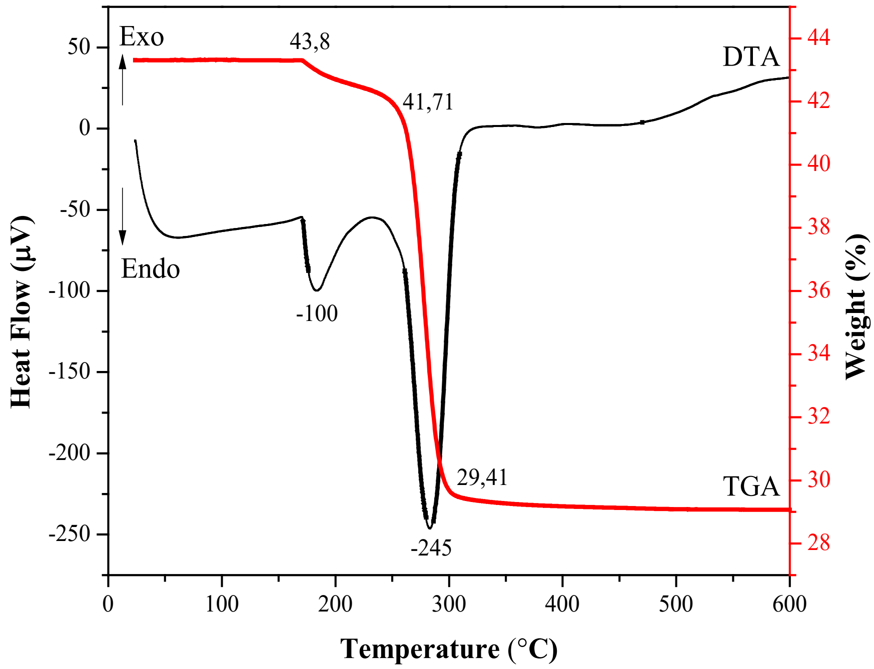

Fig. 4. TGA and DTA analysis curves of betaine-levulinate acid EILs at 1:7 molar ratio.

All parameters were measured directly from the TG curve. In addition, the peak temperature on the DTG curve (also known as Tpeak), which indicates the maximum degradation rate of the sample, at -245µV (290°C) peaks. From the results of these curves, it shows that the thermal stability of EILs is between the two initial components. It is known that dynamic scanning can only be used to measure the relative thermal stability of a compound pool [14].

3.4. Characterization of EILs using FTIR

FTIR spectroscopy was used to identify compounds, functional groups, and any structural conformational changes in the betaine-levulinic acid EILs. Figure 5 shows the FTIR spectra of betaine, levulinic acid and betaine-levulinic acid EILs with molar ratios of 1:3 to 1:7 which have shifted. This may be due to the hydrogen bond formed between the hydroxyl group of the HBD (levulinic acid) and the anion (betaine) as HBA.

Based on Fig. 5, the O-H absorption peak is generally in the range of 3000 and 3500 cm^{-1} in the infrared spectrum [21]. The results showed that betaine (3375 cm^{-1}) and levulinic acid (3367 cm^{-1}) appeared to be in a different wavenumber range (3402-3763 cm^{-1}), The O-H vibrations for EILs showed a significant shift in the absorption peak. During the formation of EILs, this wavelength shift is caused by hydrogen bonding between HBD and HBA.

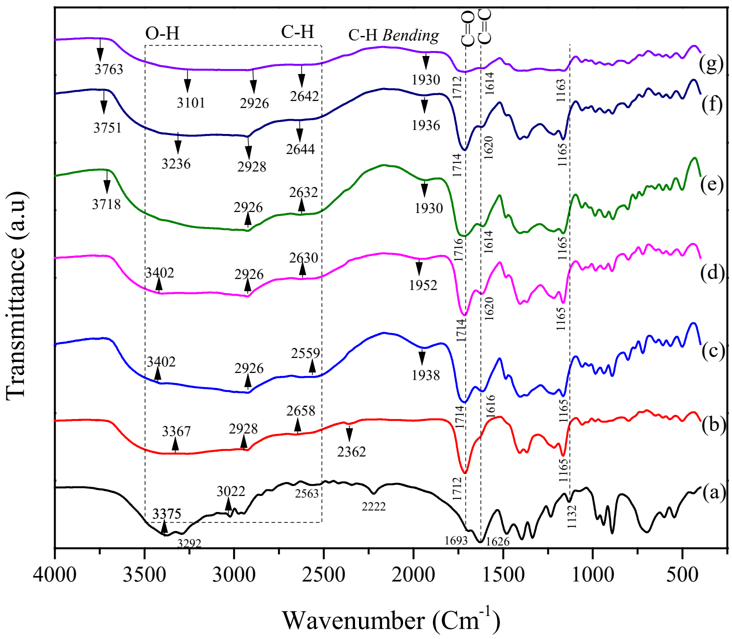

Fig. 5. FTIR spectra of Betaine (a), Levulinic acid (b), Betaine-Levulinic acid EILs 1:3 (c), 1:4 (d), 1:5 (e), 1:6 (f), and 1:7 (g).

Since the mass of levulinic acid is more dominant compared to betaine, the strength of the interaction increases with a higher betaine-levulinic acid molar ratio. Previous research shows agreement with this study, in the O-H stretching vibrations of betaine in the range of 3000-3500 cm^{-1} [22], and in levulinic acid, the results of this study are broader and stronger than those of Li et al, which is at 3100 cm^{-1}[21]. But at a ratio of 1:5 no O-H peak is observed, because the concentration of O-H functional groups in the sample is very low and weak to detect [23].

The next, there are also C-H bending vibrations that appear in betaine, levulinic acid and EILs betaine-levulinic acid molar ratio 1:3-1:7 (1930-2362 cm^{-1}), with the appearance of these absorption bands indicating that between betaine and levulinic acid compounds have a unique absorption band pattern after becoming EILs because the bond energy decreases, confirmed in previous studies that betaine has in the C-H bending absorption band [24].

In addition, the shift in the C=O vibration strain in the 1693-1716 cm^{-1} absorption band, also confirmed in research conducted [20], is in the 1705-1716 cm^{-1} absorption band which experiences hydrogen bond interactions formed between C=O on betaine and O-H on HBD (levulinate acid) that O- in the C=O group has a strong electronegativity, and when close to the positively charged H atom on O-H, intermolecular interactions occur and hydrogen bonds are formed, which results in a shift in the wavelength of the C=O group [21].

Next, the formation of betaine-levulinic acid EILs there is a stretch of C=C vibrations indicated by a shift in the betaine absorption band against EILs, namely 1626-1620 cm^{-1} which interacts. And also detected the absorption band at 1132-1165 cm^{-1} the interaction of N^+ on betaine with O^- on levulinate. The vibration of N-O is stronger than the betaine molecule which is closed on the surface of levulinic.

In addition, levulinic acid as an HBD is an L-glucuronic acid and fructose acid, which indicates that it contains highly reactive carbonyl and carboxyl groups and can carry out various reactions, including redox reactions, esterification, substitution, polymerization, chiral synthesis, resolution, and so on. Levulinate acid is also one of the most promising new platform materials due to its reaction properties [25]. The presence of carbonyl groups on levulinate acid allows it to interact with other carboxylic functional groups on betaine as hydrogen bond acceptors through molecular interactions, such as H or π-π bonds in the formation of EILs [21].

3.5. Analysis of EILs using CV

In knowing the feasibility of a material used as a redox electrolyte is to know the width of the electrochemical windows (electrochemical windows) of the compound, the redox potential can be determined using CV electrochemical techniques [26], the EILs compound betaine-levulinate acid is with a molar concentration ratio of 1:3-1:7, were tested using CV with a platinum electrode as the working electrode, platinum wire as the auxiliary electrode, Ag/AgCl calomel electrode as the comparison electrode, and the measurement limit was determined in the region of ± 0.9 V, and under atmospheric pressure of Nitrogen (N2), both compounds showed wide window results.

The electrochemical window is one of the most important characteristics that must be identified in mediums and electrolytes, especially those used in electrochemical applications. This term is generally used to indicate the range/potential difference at which a substance becomes inert (neither oxidized nor reduced) [27]. With the curve showing a reversible redox process in Fig. 6. The anodic current peak corresponds to the anodic oxidation of the analyte and the cathodic current peak corresponds to the reduction process of the oxidation product observed in the reverse cycle after a change in electrode polarity [28].

The results of this study show that the CV curve has consistent stability, but a narrower electrochemical window width, that in the case of ionic liquids, electrochemical stability mainly depends on the resistance of reduced cations and oxidized anions [29]. The more easily a compound undergoes redox reactions, the smaller the electrochemical window width [29].

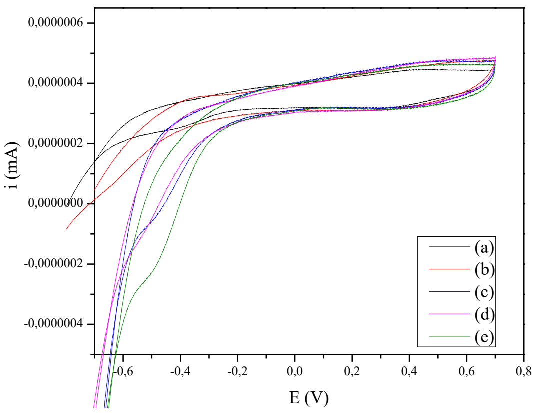

Fig. 6. Cyclic Voltammetry Curves of Betaine-levulinic acid EILs 1:3 (a), 1:4 (b), 1:5 (c), 1:6 (d), and 1:7 (e).

3.6. EILs Analysis of the techno-economy

A techno-economic evaluation was conducted to determine the use of EILs for lixiviant against red mud as a viable option. During this assessment, economic parameters such as Gross Profit Margin (GPM), Payback Period (PBP), Break-Even Point (BEP), Break-Even Capacity (BEC), Internal Rate Return (IRR), Cumulative Net Present Value (CNPV), Return On Investment (ROI), and profitability index (PI) were calculated and analysed. The calculations are done with Microsoft Excel. In addition, these calculations require information on prices, specifications, and costs of raw materials, as well as utilities. Some online trading platforms, such as Alibaba, provide this data shown in Fig. 7. To the research of Nandiyanto et al. [30], Noorlela et al. [31] and Ragadhita et al. [32] calculated these economic parameters.

GPM is calculated by subtracting sales from raw material costs. PBP is the year in which CNPV/TIC equals zero. BEP is calculated by dividing fixed and variable costs by fixed and variable costs. BEC is calculated by dividing BEP by the unit production capacity over a period of time. The following equation 1 is used to calculate IRR:

$$\text{IRR} = \sum_{t-1}^{t} \frac{C_t}{(1+r)^t} - C_0 \quad (1)$$

where Ct = Net cash inflow during period *t*, r = Discount rate, *t* = Number of time periods, and C0 = total initial investment cost.

CNPV is calculated by summing the NPV of the initial project establishment with the NPV at that time. NPV is calculated by multiplying the cash flow by the discount factor. ROI is calculated by dividing total profit by investment cost. PI is calculated by dividing the difference between sales and production costs by sales (profit-to-sales) or investment (profit-to-TIC).

Figure 7 illustrates the profitability of the techno-economically analysed process as a lixiviant to red mud and values are listed in Table 1.

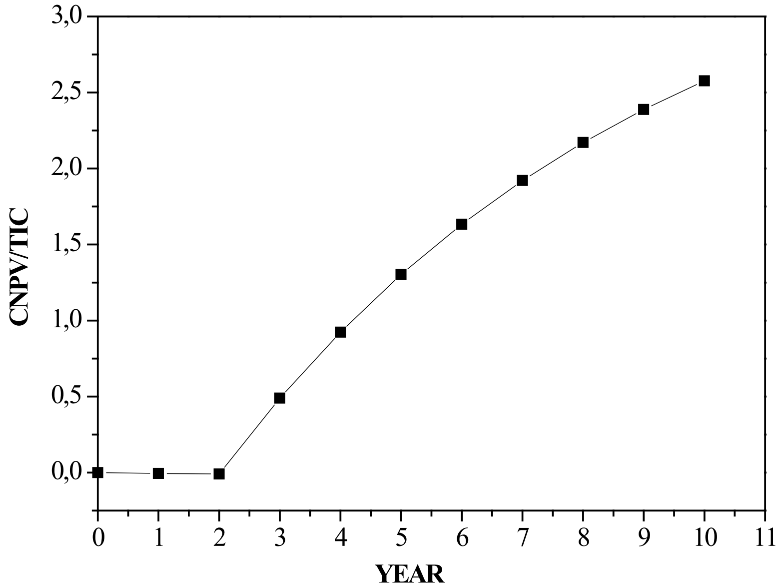

Fig. 7. Ideal conditions for CNPV/TIC sustainability.

Table 1. CNPV values under ideal conditions.

Parameter Ekonomi	EILs Betain-Asam Levulinate
GPM (IDR/kg/Year)	Rp 35,750,342,956
PBP (Year)	2.1
BEP (kg)	288.6305729
BEC (%)	0.431
IRR (%)	10.09
Final CNPV/TIC (%)	2.58
ROI (%/Year)	4.72
ROI total	84.97
PI profit-to-sales (%)	3.4
PI profit-to-TIC (%)	3.53

Profit declines slightly in the first to second year due to the cost of purchasing equipment, construction, and other costs at the beginning of this year. Then, at the beginning of the second year, the payback period (PBP) begins to occur, and profits begin to be earned. Overall, the EILs synthesis process using betaine and levulinic acid is considered profitable due to the positive change in CNPV/TIC rates [33]. Broadly speaking, the economic evaluation parameters under ideal conditions are positive.

4. Conclusion

Betaine (HBA) - levulinic acid (HBD) EILs have been successfully synthesized using Solv metallurgical method. The resulting EILs showed physical characteristics of a viscous, homogeneous, and odourless liquid, and DSC analysis confirmed the formation of a eutectic point with the lowest freezing point at a molar ratio of 1:7 (-34°C). TGA-DTA curve test results showed that the thermal stability of EILs was between the two starting components with a mass loss of 2.1%. FTIR characterization results showed conformational changes in hydrogen bonds formed between hydroxyl groups of HBD (levulinic acid) and anion (betaine) as HBA evidenced by the absorption band area of 1132-3763cm-1. Analysis of EILs using CV has physicochemical properties (electrochemical window) which shows good electrochemical stability results with the formation of regular cyclic patterns. And the economic evaluation analysis of the EILs synthesis process using betaine and levulinate acid as lixiviant against red mud is considered favourable due to positive changes in CNPV/TIC rates.

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