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Liquid-liquid Extraction of Lactic Acid from Aqueous Medium Using Menthol-lauric Acid and Thymol-lauric Acid Deep Eutectic Solvent

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***Abstract**: Chemistry is paying more attention to deep eutectic solvents, a kind of environmentally benign solvent that may be used to extract and separate target molecules from a variety of samples. This paper focuses on the use of non-ionic hydrophobic-based deep eutectic solvents (DES) for the extraction of lactic acid from an aqueous medium and to determine the physiochemical properties that make them unique from other extraction solvents. According to the results of this work, a ternary phase diagram composed of menthol and lauric acid (1:1) and thymol and lauric acid (1:1) was determined at 298.15 K and atmospheric pressure. The tie lines show that the raffinate phase contains no DES and the extract phase contains no water in it. This is an important advantage of DES as a solvent compared to organic solvents since it could reduce the number of purification steps in the extraction unit and thus reduce its operating cost. The synthesised DESs' component FTIR spectra were examined. The findings revealed shifts (stretch and vibration) that may be related to interactions, structural modifications, and the development of chemical bonds between the bands at 3242 (cm^{-1}) and 3417 (cm^{-1}). The density values of DES A range from 0.897 to 0.853 g/cm^3, and those of DES B fall between 0.936 and 0.837 g/cm3. The synthesised DESs' surface tensions were tested; DES A displayed a greater surface tension of 31.14 mN/m, while DES B displayed a lower surface tension of 29.29 mN/m. These surface tension values fall within the literature range of 20–60 mN/m for DESs; hence, they can be used as a potential alternative solvent to conventional organic solvents for lactic acid extraction owing to their attractive and eco-friendly properties. The systems displayed a higher extraction efficiency of 99%, indicating the potential use of DESs as solvents for the separation of lactic acids from an aqueous medium.*

Keywords: Deep eutectic solvents, characterization, lactic acid, menthol, thymol, lauric acid.

1. INTRODUCTION

Concern over creating a viable and efficient method for recovering fermentable lactic acid is emerging in response to the rising demand for the substance [24, 30]. Lactic acid (LA) is a water-soluble organic compound produced via the breakdown of carbohydrates and is widely used in the production of polylactic acid (PLA) which is a bio-based polymer, which has received extensive attention, both in academia and industrially in the last 20 years [22], cosmetics, pharmaceuticals, food, and drinks, as well as the growing use of eco-friendly packaging materials [25]. It has a general molecular formula of $CH_3CH(OH)COOH$, is colourless in liquid form and miscible with water. In chemical terms, lactic acid (LA) is 2-hydroxypropanoic acid. It is sometimes referred to as milk acid and is the most prevalent carboxylic acid in nature, with uses in numerous sectors [2]. lactic acid is one of the important chemicals utilized in the polymer industry [28] and Lactic acid is a fundamental molecule that is utilized as a feedstock for the fermentation process that produces a variety of products, according to [15, 17].

Different approaches have been tested up to this point for recovery of LA from fermentation broth to cut production costs, the volume of effluents produced, and ultimately the environmental impact [14]. Some of the technologies that have been employed as an alternative to the traditional process include precipitation, adsorption, solvent extraction, reactive distillation, and membrane separation processes [16].

The traditional method of purifying lactic acids by precipitating them as calcium lactate yields a lot of gypsum ($CaSO_4$) more than what LA produces. This leads to low productivity and yield in LA, as well as environmental issues. As a result, the process has made it difficult to produce lactic acid economically and commercially [24]. According to the literature, solvent extraction is the best option and one of the best alternatives for purifying lactic acid; however, the high toxicity, expense, and non-biodegradability of conventional organic extraction agents limits solvent extraction efficiency, which means that a major obstacle to lactic acid productivity and yield is the development of efficient separation and purification methods that lower the cost of manufacturing LA from the fermentation broth [25]. Despite the use of these methods, the goal of this research is to increase lactic acid yield using low-cost, ecologically research methods and the primary focus of green analytical sample preparation methods is the elimination of hazardous and volatile organic solvents [1, 35].

Deep eutectic solvents (DES) have been intensively explored and used in sample preparation techniques during the last decade [3]. Until recently, the majority of DES produced were hydrophilic, preventing their usage in aqueous sample extraction [23, 32]. Nonetheless, the development of hydrophobic deep eutectic solvents (HDES) and their applications has expedited study. Many works in the literature have been exploring the suitability of the different forms of DES applications in different processes. Some of these include searches focusing on the identification of the stable DES for a potential application. [33]. The unique properties of HDES, such as density, viscosity, acidity or basicity, polarity and volatility, and good extract abilities for various target analyses, make them promising substitutes for traditional organic solvents used in sample preparation. These properties can be modified by carefully choosing the components that form the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), [11, 34]. Furthermore, the possibility of HDES synthesis of non-toxic ingredients ensures that HDES meets all green analytical chemistry standards [23, 31]. This study will examine the practical applications of HDES, which can be synthesised from menthol, thymol, and lauric acid and are suitable candidates to generate hydrophobic, affordable, and sustainable solvents by forming eutectic mixtures, that can be used to extract lactic acid from aqueous samples.

2. EXPERIMENTAL SECTION

2.1 Material

Lauric acid with ⩾98% purity, lactic acid with ⩾ 85% purity, menthol with ⩾ 98% purity, and thymol with ⩾ 98% purity was bought from Sigma Aldrich reagent and was used s received. The water used was pure, doubled distilled water from the chemical engineering department

2.2 Preparation Method

The DES was prepared by combining a 1:1 mole ratio of menthol as the hydrogen bond acceptor and lauric acid as the hydrogen bond donor and the second mixtures was a combination of a hydrogen bond donor (lauric acid) and a hydrogen bond acceptor (thymol) which was placed in a beaker and heated at 50 ºC for 15 min and stir at 200 rpm with a magnetic stirrer until a homogenous colorless and orange liquid of the two mixtures were formed. These mixtures were allowed to cool to a room temperature and stored under an atmospheric pressure until used. The both eutectic mixtures stayed in liquid state for 6 months at room temperature without forming any crystals. The final combinations' composition and purity were verified using FTIR (SHIMADZU FTIR- 8400S) and Autoclave.

Figure 1: Synthesis of the eutectic mixture and how water causes it to phase split. Thymol and lauric acid (both solids), the eutectic mixture of the two (1:1), and the eutectic mixture after adding water

2.3 FTIR Measurement

FTIR measurements were carried out using a PerkinElmer FT 9700 FTIR spectrometer with a single reflection ATR cell. At room temperature, the spectral area data were recorded between 4000 and 500 cm^{-1}.

2.4 Physiochemical Properties

Viscosity, density, surface tension, pH, melting point, ionic conductivity, sensitivity and toxicity tests of the eutectic mixtures were carried out in the temperature range of 298.15 to 358.15 K and at atmospheric pressure. Ametek Brookfield DV2T touch screen automated viscometer, densimeter, Fisher Scientific acumen AE150 digital pH meter and Fisher brand conductivity meter were used to carry out these properties. There is a ±0.02 K temperature uncertainty. The dynamic viscosity's relative uncertainty is ±0.45%, whereas the density's absolute uncertainty is $\pm 0.0005\ g\cdot cm^{-3}$.

2.5 Liquid-Liquid Equilibrium

For the systems under study, the LLE data were found to be 298.15 K in a 100 ml conical flask. The mixtures of lactic acid with an initial concentration of (1-10%) and DES were prepared using a precision of the Mettler 205 balance of $\pm 1 \times 10^{-4}$ g. Less than 0.0005 was the calculated uncertainty of the feed in mole fraction. To guarantee that the two phases were completely separated, the mixture was agitated vigorously for 5 hours and then allowed to attain the saturation equilibrium for 24 hours. The water-rich phase's (raffinate) components were ascertained using a 752N UV-spectrometer and results are shown in Table 2.

3. RESULT AND DISCUSSION

Important solvent characteristics, including density, surface tension, melting point, pH, conductivity, sensitivity test, and viscosity, were examined in eutectic mixes of menthol and lauric acid, thymol and lauric acid, to assess their viability as extraction solvents.

3.1 The FTIR Analysis

It is crucial to understand the interactions between menthol and lauric acid as well as thymol and lauric acid in the two eutectic combinations made in this work. FTIR tests were conducted for that reason on eutectic mixtures, pure lauric acids, pure thymol, and pure menthol. Figure 2 and Figure 3 respectively, show the overlapping FTIR spectra obtained for the menthol: lauric acid eutectic mixture, thymol: lauric acid eutectic mixture, and their corresponding components.

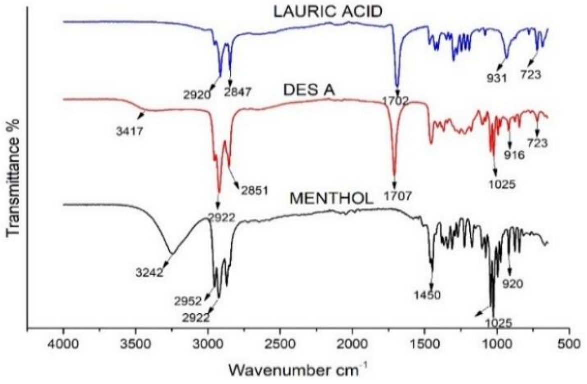

Figure 2: FTIR spectra of the pure menthol, lauric acid, and the eutectic mixture of menthol and lauric acid (1:1 molar ratio)

From Figure 2, the hydrogen bond donor used in menthol-lauric acid mixtures has a carboxylic acid group in its structure that exhibits a representative band carbonyl group in the spectra between 1700 - 1702 cm^{-1}. Conversely, only one representative band, belonging to the hydroxyl group, at around 3242 cm^{-1} is seen in the FTIR spectra of the hydrogen bond acceptor, menthol. Furthermore, by forming hydrogen bonds between the hydrogen bond donors and the menthol, a novel molecule, was formed, as confirmed by FTIR studies. it is clearly seen that the intermolecular hydrogen bond interaction between menthol and lauric acid is seen in the carboxyl group area of the FTIR spectra of the eutectic mixtures Figure 2 shows that the carbonyl band from the HBD and HBA was initially positioned at low wavenumber values (1450 cm^{-1} and 1702 cm^{-1}), and it broadens and changes to the high values (1703 cm^{-1}) in the eutectic combination for menthol: lauric acid. This is a clear sign of the development of a new hydrogen bond, indicating the formation of a new molecule. The physical states of the compounds, such as the eutectic mixture consisting of menthol and lauric acid, can further support these findings as Initially, both of these compounds are solid, but following DES formation, a liquid is obtained.

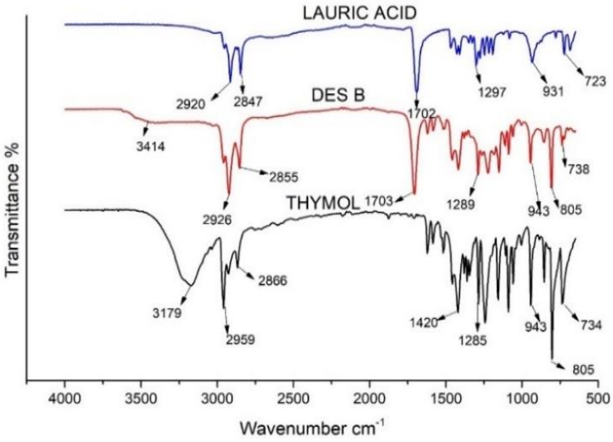

Figure 3: FTIR spectra of the pure Thymol, lauric acid, and the eutectic mixture of Thymol and lauric acid (1:1 molar ratio)

From Figure 3, the hydrogen bond donor used in thymol-lauric acid mixtures has a carboxylic acid group in its structure that exhibits a representative band carbonyl group in the spectra between 1400-1700 cm^{-1}. In contrast, the FTIR spectra of the hydrogen bond acceptor, thymol, show only one characteristic band, which is located at around 3179 cm^{-1}. This band is associated with the hydroxyl group. Furthermore, by forming hydrogen bonds between the hydrogen bond donors and the thymol, a novel molecule, was formed, as confirmed by FTIR studies. The carboxyl group area of the FTIR spectra of the eutectic mixtures is where the intermolecular hydrogen bond interaction between the hydrogen bond donors and thymol is most prominent. Figure 3, shows that the carbonyl band from the HBD and HBA was initially positioned at low wavenumber values (1420 cm^{-1} and 1702 cm^{-1}), and it broadens and changes to the high values (1703 cm^{-1}) in the eutectic mixture for the thymol: lauric acid eutectic mixture. This is a clear sign of the development of a new hydrogen bond, indicating the formation of a new molecule.

3.2 Physicochemical Properties

Viscosity, density, surface tension, PH, melting point, sensitivity and toxicity test are of a solvent's most crucial characteristics since they have an impact on mass transport phenomena, which in turn affects the solvent's applicability for different applications and their data are plotted as shown in Figure 4, Figure 5, and Figure 6.

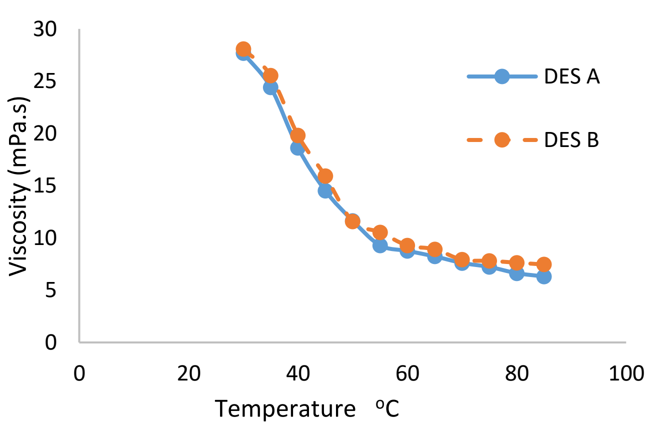

Figure 4: Variation of Viscosity with temperature for hydrophobic DES A (menthol: lauric acid) and DES B (Thymol: lauric acid)

When considering the molecular interactions and electrostatic attraction between the liquid components, a solvent's viscosity is determined. Therefore, DES with low viscosities is very essential for extraction application. At a temperature of 30 ºC, the DESs showed a relatively low viscosity of 27.67 mPa.s for DES A and 28.068 mPa.s for DES B owing to the low depressions in the melting point which makes the viscosity appealing for many applications Increase in temperature from 30 ºC – 85 ºC, the viscosity of the DESs decreases exponentially from 27.67 mPa.s to 6.315 mPa.s for DES A and from 28.068 mPa.s to 7.46 mPa.s for DES B as shown in Figure 4.

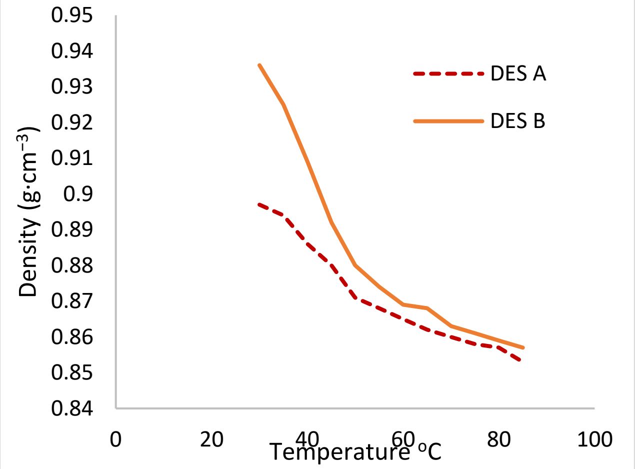

Figure 5: Variation of density with temperature for hydrophobic DES A (menthol: lauric acid) and DES B (Thymol: lauric acid)

When it comes to DES's miscibility with other liquids and solvent diffusion, its density during extraction is a key factor. When mixed with other liquids, the majority of hydrophobic DESs show reduced density and base on the density differential, DESs' immiscibility with water determines how effective their extraction is. DES B has a higher density of 0.936 g·cm^{-3} to that of DES A with density of 0.897 g·cm^{-3} at room temperature. And it can be observed from Figure V that the density is temperature dependant. as density decrease with increase in temperature from 30 ºC - 85 ºC.

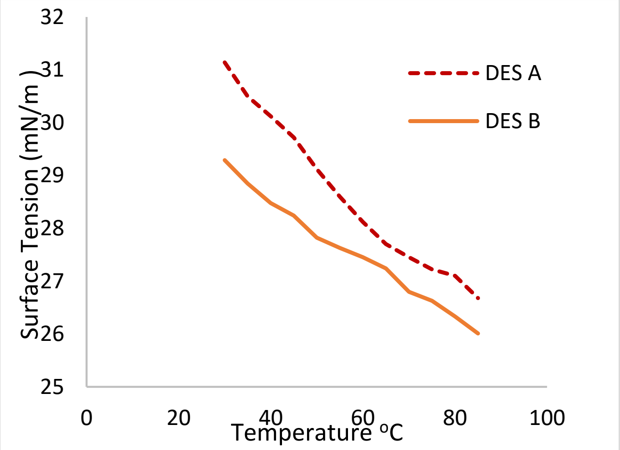

Figure 6: Variation of surface tension with temperature for hydrophobic DES A (menthol: lauric acid) and DESB (Thymol: lauric acid)

Surface tension is a measure of the intermolecular forces at the interface between two immiscible liquids. Surface tensions between 20-60 mN/m is effective for extraction applications. As shown in Figure , DES A has a surface tension of 31.14 mN/m and DES B with surface tension of 29.29 mN/m which are within the literature range. It is also temperature dependent.

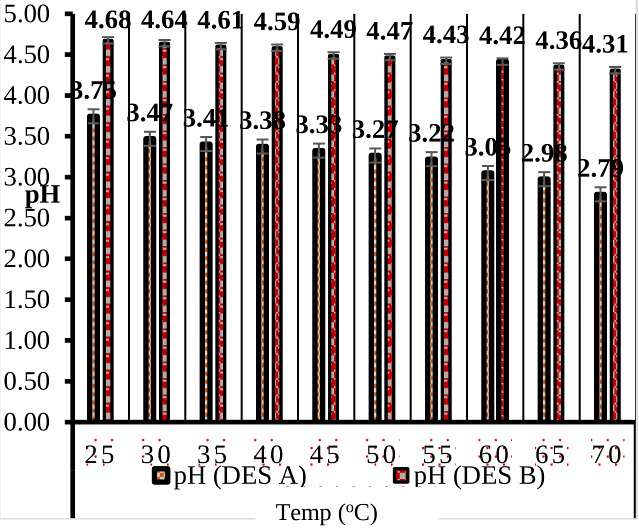

Figure 7: Variation of pH with temperature for hydrophobic (menthol: lauric acid) and DES B (Thymol: lauric acid)

The chemical potential of hydrogen and temperature determine a solvent's pH [38]. The way the ions interact with other species in the solvent affects the chemical potential. Hydrogen bond interaction with other components determines the hydrogen chemical potential of DESs; the greater the relationship between DES and another component, the higher the component's extractability by DES [10]. As shown in Figure the pH of the DES showed a slight decreasing effect with increase in temperature from 4.68 to 4.31 for DES B and 3.75 to 2.79 for DES A at 30 ºC at 85 ºC, this could be explained by the fact that the degree of association increases with temperature, increasing molecular vibrations and, ultimately, the hydrogen bond donor's (HBD) degree of association with other components. As a result, the chemical potential of hydrogen lowers, and consequently, pH.

Table 1: The melting and conductivity properties of DESA (menthol: lauric acid) and DESB (thymol: lauric acid)

Component	**Melting points (ºC)**	**Literature value (ºC)**	**Conductivity** (S/m)
DESA	21 ºC	22.25 ºC	0
DESB	24 ºC	25.79 ºC	0

From the literature DES with a melting point lower than 50 ºC are more attractive [12] and from Table 1 shows that the both DES has lower melting point than their individual melting, leading to less viscous form of DESs, which means less or no additional heat source is needed reducing cost of process and making them stable in the liquid state at room temperature.

The conductivity of non-ionic hydrophobic deep eutectic solvents was observed to be 0 from 30 ºC – 85 ºC showing that there is no ionic conductivity which is due to the fact that non-ionic hydrophobic deep eutectic solvents do not contains mobile charge particles such as ions and they are made up of neutral molecules and do not conduct electricity, which is one of the advantages of using hydrophobic deep eutectic solvent as an alternative to traditional ionic solvents as they do not have issues with ionic contamination and can be used in electrochemical systems that use non-ionic conductors.

Table 2: Toxicity and sensitivity test of the synthesized (hydrophobic) DESs using well diffusion methods

	Sample concentration (µ ml)				Species	Remark
DES A	100	50	25	12.5	Staphylococcus	+ (NI)
	2.1	1.3	1.2	1.1	Pseudomonas	+ (NI)
	3	1.7	1.4	1.3	Bacillus	+ (NI)
	2.5	8.7	1.2	8	E- Coli	+ (NI)
	2.4	1.8	1	1	Salmonella	+ (NI)
	2.3	1.7	1.3	1	listeria	+ (NI)
	2	1.5	1.3	1	Staphylococcus	+ (NI)
DES B	2.5	2	1.8	1	Staphylococcus	+ (NI)
	1.9	1.7	1.4	1.1	Pseudomonas	+ (NI)
	2.2	1.3	1.3	1.1	Bacillus	+ (NI)
	3	1.7	1.4	1	E- Coli	+ (NI)
	2.5	1.5	1.4	1.2	Salmonella	+ (NI)
	2.1	1.3	1.2	1.1	Listeria	+ (NI)

Before considering their applications of DES for extraction of lactic acid, it is necessary to understand its toxicity profile. And from Table 2, it can be seen that the synthesized DESs showed lower toxicity to the tested bacteria investigated based on the Clinical Laboratory Standard International (CLSI) indicating that the studied DESs were less toxic since the zone of inhibition diameter were less than 10 mm. Therefore, they could be regarded as safe and still within the range for the applications in food, pharmaceutical industries.

3.3 Liquid- Liquid Experimental Data

Table 3 and 4 reports the LLE experiment results for the ternary systems {Water + Lactic + DES} at room temperature (298.15 K) and atmospheric pressure. Figure VIII-IX uses a ternary plot to display the appropriate triangular phase diagrams for these systems. It was established that samples from phases with high water content were DES-free, this is a kay advantage of using DES as solvents for extraction when compared to organic solvents because fewer purifying stages will be required in the extraction unit, which would save operating costs. [18]. Lactic acid is completely miscible with water and somewhat immiscible with DES, as Figures 8 and 9 demonstrated. Secondly, DESs and water are immiscible. These ternary phase diagrams, with their broad immiscibility zone between water and DES, match to the Type 2 category in the classification established by Sorensen and colleagues. Furthermore, the positive slope of the tie-lines shows that, following extraction, lactic acid is far more soluble in DES than water. Nearly all of the triangle diagrams have tie-lines, indicating the possibility of a successful compound separation from aqueous phase employing the DESs under study.

Table 3: Experimental LLE data in weight fraction for the ternary systems of (DESA + Lactic acid + water) at temperature 298.15 K and atmospheric pressure along with the solute distribution ratio (β) and extraction efficiency (%EE) values calculated using Equations 1 and 2, respectively

Initial concentration of lactic acid (weight%)	Weight of LA IN raffinate phase (g)	Weight of LA in extract phase (g)	β	%EE
0.1	0.07451	0.00505	26.4	99.62
0.2	0.08576	0.01691	23.4	99.58
0.3	0.10872	0.02725	27	99.65
0.4	0.20315	0.02994	19.1	99.53
0.5	0.24901	0.03766	19	99.52
0.6	0.35494	0.03911	15.9	99.45
0.7	0.39967	0.04679	15.8	99.44
0.8	0.46827	0.05197	15.6	99.42
0.9	0.51186	0.05957	15.6	99.4
1.0	0.54267	0.06828	15.50	99.38

Table 4: Experimental LLE data in weight fraction for the ternary systems of (DES B + lactic acid +water) at temperature 298.15 K and atmospheric pressure along with the solute distribution ratio (β) and extraction efficiency (%EE) values calculated using Equations 1 and 2, respectively

Initial concentration of lactic acid (weight%)	Weight of LA IN raffinate phase (g)	Weight LA in extract (g)	β	%EE
0.1	0.05035	0.00739	39.77	99.73
0.2	0.07376	0.01745	27.9	99.62
0.3	0.08488	0.02855	36.16	99.71
0.4	0.14321	0.03473	28.25	99.64

Initial concentration of lactic acid (weight%)	Weight of LA IN raffinate phase (g)	Weight LA in extract (g)	β	%EE
0.5	0.17722	0.04322	28.01	99.64
0.6	0.27030	0.04584	21.56	99.54
0.7	0.36325	0.04847	18.44	99.46
0.8	0.43169	0.05343	17.59	99.44
0.9	0.51186	0.05723	17.18	99.44
1.0	0.51835	0.7200	16.12	99.39

$$\text{Distribution Coefficient } (\beta) = \frac{\text{LA conc. in Upper phase } (\frac{g}{ml})}{\text{LA conc. in Lower phase } (\frac{g}{ml})} \qquad 1$$

$$\text{Extraction Efficiency } (\%EE) = \frac{M_0 - M_1}{M_0} \times 10 \qquad 2$$

From equation 1, $\text{LA conc. in Upper phase } (\frac{g}{ml})$ is the concentration of lactic acid in the upper phase (DES rich phase) and $\text{LA conc. in Lower phase } (\frac{g}{ml})$ is the concentration of lactic acid in the lower phase (water rich phase). From equation 2, M_o is the initial weight percent of lactic acid and M_1 is the final weight percent of lactic acid.

Equations 1 and 2 were used to determine the solute distribution ratios (β), which give a quantitative understanding of the distribution in the equilibrium phase based on tie-line compositions.

The potential utility of the investigated DESs as solvents for the liquid-liquid extraction of lactic acids from the aqueous medium was assessed using these two equations. For the two ternary systems under study, distribution coefficient values are greater than 1, suggesting that the investigated DES could be employed as solvents for lactic acid separation from aqueous medium and that less solvent will be required for the extraction. Table 3 and 4 reveals that distribution coefficient values decrease with increasing the concentration of Lactic acid. In addition, at 0.3 (wt.%) concentration of lactic acid, DES A has the highest extraction efficiency and DES B with high distribution coefficient at 0.1 (wt.%) concentration of lactic acid. Both DESs has the high extraction efficiency of 99% which made the both solvents more efficient in the extraction of lactic acid from aqueous medium.

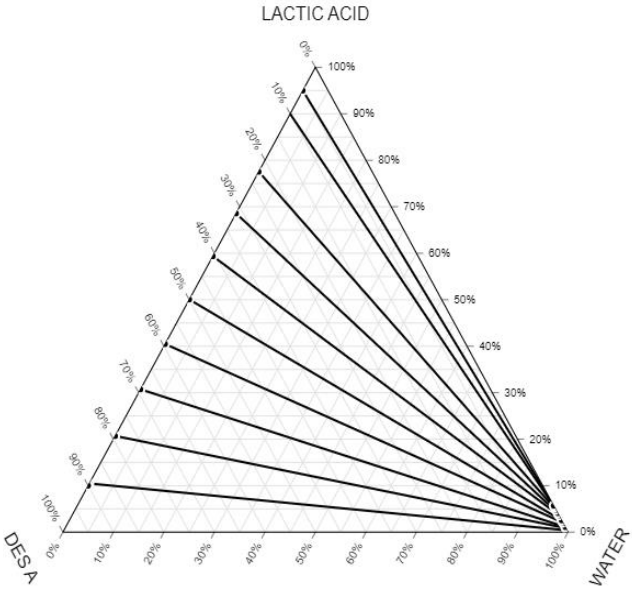

Figure 8: Tie-lines for ternary mixture of {Lactic acid + water + DESA} at temperature 298.15 K

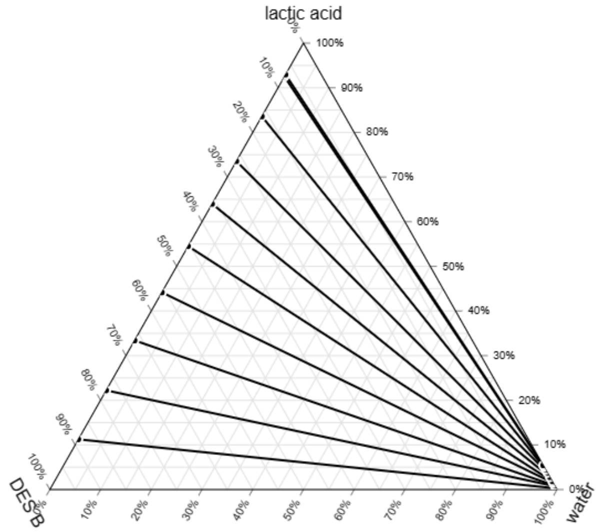

Figure 9: Tie-lines for ternary mixture of {Lactic acid + water + DESB} at temperature 298.15 K

4. CONCLUSION

In this work, non-ionic hydrophobic deep eutectic solvents with components from a natural resource were studied. These new solvents are eutectic mixtures composed of menthol, thymol and lauric acids in 1:1 proportion with a low melting point of 21 ºC and 23 ºC for both DESs lower than their individual components. Contrary to deep eutectic solvents, these two natural eutectic solvents presented low viscosities of 27.67 mPa. s and 28.068 mPa. s and densities of 0.936 g·cm^{-3} and 0.897 g·cm^{-3} lower than water and low surface tension of 31.14 mN/meter and 29.29 mN/m. The synthesized DESs showed lower toxicity to the tested bacteria investigated, making them safe and still within the range for the applications in food, pharmaceutical industries. Despite the fact that these eutectic mixtures are composed of naturally occurring hydrophilic acids, they are immiscible with water, which confers them a privilege place among the green solvents, which are usually very hydrophilic. the experimental LLE data for two ternary systems (water + Lactic acid +DES A) and (water + Lactic acid + DES B) were determined at temperature 298.15 K and at atmospheric pressure. From the compositions of the conjugate phase in the equilibrium, the extraction efficiency and solute distribution ratio were calculated. The solute distribution ratio values are higher than unity for the two studied ternary systems, which confirms that the studied DES could be used as potential solvents for the separation of lactic acid from aqueous medium.

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