

Research Article

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Liquid–Liquid Extraction of Linalool from Methyl Eugenol with 1-Ethyl-3-methylimidazolium Hydrogen Sulfate [EMIM][HSO₄] Ionic Liquid

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Abstract: The liquid–liquid equilibrium (LLE) data for a ternary system {methyl eugenol + linalool +1-ethyl-3-methylimidazolium hydrogen sulfate [EMIM][HSO₄]} (Meu-Lin-IL) were measured at 298.2 K and atmospheric pressure. The Othmer–Tobias correlation was used to verify the reliability of the experimental tie-line data. The solubility curves were obtained using the cloud point titration indicating the liquid-liquid equilibrium of the ternary system was in Type II class where two immiscible curve pairs were attained. Distribution coefficients, separation factors and selectivity were calculated for the immiscibility regions. The calculated results were compared with the experimental data. Characterization studies were performed by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and proton nuclear magnetic resonance spectroscopy (¹H-NMR) techniques.

Keywords: [EMIM][HSO₄]; Extraction; Ionic liquid; Linalool; Methyl eugenol.

1 Introduction

Ionic liquids (ILs), green solvents, are environmentally friendly solvents [1] and they have gained considerable importance in recent years because of their superior properties such as non-volatility [1, 2], solubility in a broad range of compounds and excellent thermal and chemical stability [2]. Different separation techniques are

present such as membrane separation [3], pervaporation [3] and extraction [4]. Because of the significant advantages of ionic liquids, they have a great potential to be investigated for extraction and other separation processes [5, 6]. Detailed economic analysis of hydrogen sulfate based ILs was performed [7]. It was reported that large volume-IL based applications may be commercially feasible and also, ILs can be as inexpensive as typical organic solvents [7]. Studies on the liquid-liquid extraction with ionic liquids showed that ionic liquid is an efficient solvent for the separation process. [8-14]. ILs can easily be synthesized with a conceivable cost [9] and ILs also have advantages in terms of economy such as decrease in purification steps and reduced cost of process [14]. Because of the unimportant vapor pressure and an acceptable range of toxicity, the use of ionic liquids as solvent in liquid extraction processes has gained much interest [9]. Arce et al. [9] performed a LLE study of limonene-linalool-1-ethyl-3-methylimidazolium ethyl sulfate ternary system. They measured equilibrium data at 298.15 K and 318.15 K. Distribution ratio of linalool and selectivity were calculated and found that slightly higher values of these parameters were obtained at 298.15 K. A solutropy was observed where the slope of tie-lines varied from negative to positive values as linalool content increased. Distribution coefficients were lower than 1 in the low-linalool region and greater in the high-linalool region because of a solutropic phenomenon. Selectivity decreases with an increase in linalool composition. In another study of Arce et al. [15] where they studied limonene+linalool+2-aminoethanol at different temperatures, they concluded that the studied temperatures had no effect on LLE. Gramajo de Doz et al. [16] studied LLE of limonene +linalool+water system at the temperatures 298.15 K, 308.15 K, and 318.15 K. They concluded that this ternary system has a very low solubility for limonene-water and linalool-water binary system at the studied temperatures. They stated that they could not determine distribution coefficient, separation

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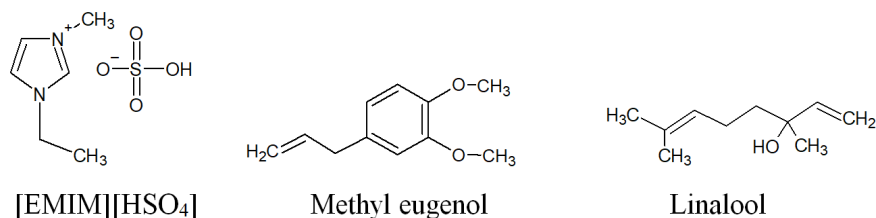


Figure 1: Structure of [EMIM][HSO₄], methyl eugenol and linalool.

factor, and selectivity parameters since the experimental results were not accurately adequate because of very low solubility of limonene and linalool in water [16]. Gonçalves et al. [17] studied LLE of limonene-linalool-alcoholic solvents. They used ethanol with different water content and found that the increase of water content in ethanol caused a decrease in the extraction of oxygenated components (i.e., linalool). Therefore, higher ability of extraction was reached in the case of lower water content. Lago et al. [18] investigated LLE ternary system of three 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids (with ethyl-, hexyl-, or decyl- alkyl groups) formed by essential oils (limonene and linalool) at 298.15 K. They [18] stated that all three systems show a Type II behavior. Solute distribution ratio and selectivity parameters were calculated to evaluate the efficiency of ILs for extraction. While distribution ratios were lower than 1, selectivity values were higher than 1. To the best of our knowledge, there is no report on the separation of methyl eugenol + linalool essential oil components except a study where kinetic and diffusion parameters were investigated for solvents and also for methyl eugenol + linalool mixtures using synthesized copolymers of poly(dodecyl methacrylate-co-methyl eugenol) and poly(dodecyl methacrylate-co-methyl chavicol) gels [19].

Structures of [EMIM][HSO₄], methyl eugenol and linalool are shown in Figure 1. Methyl eugenol and linalool are essential oil components obtained from sweet basil including to methyl eugenol-linalool chemotype [20]. In Turkey (İzmir and Çanakkale) methyl eugenol-linalool chemotype is cultivated where methyl eugenol and linalool are the highest components in sweet basil essential oil of this chemotype [21]. The present study focused on the use of 1-ethyl-3-methylimidazolium hydrogen sulfate [EMIM][HSO₄] as an ionic liquid for the liquid-liquid extraction of linalool from methyl eugenol + linalool mixture. Detailed characterization studies were also performed. The obtained equilibrium data are in Type II class which is found rarely in literature [18, 22-24].

2 Experimental

Methyl eugenol (≥98%) and linalool (≥97%) were obtained from SAFC Sigma- Aldrich Chemie GmbH (Steinheim). 1-ethyl-3-methylimidazolium hydrogensulfate (> 99%) was supplied by Io-li-tec (Ionic Liquid Technologies GmbH). FTIR bands were recorded by using a Jasco ATR PRO ONE FT/IR-4700 Fourier Transform Infrared Spectrometer. The ¹H-NMR spectra were recorded on a Varian UNITY INOVA 500MHz NMR spectrometer in CDCl₃. Thermal gravimetric analysis was carried out using a simultaneous DTA-TGA apparatus (Shimadzu DTG-60) in a nitrogen atmosphere (20 mL/min) at a 10°C/min heating rate from 25 to 500°C.

Cloud point method [25] was used to determine the solubility curves of the system. Binary mixtures of either (methyl eugenol + linalool) or (linalool+[EMIM][HSO₄]) prepared at different mass fractions were placed inside the jacketed equilibrium glass cell and titrated by the third component. Isothermal conditions were provided by using circulating water from a water bath (NUMAN, SM I Model) which involved a PID temperature controller to keep the equilibrium cell constant at 298.2 K. Tie-line data were obtained using mixtures of each component with known masses lying within the heterogeneous gap. The mixtures were stirred vigorously in an incubator (SPX Model) with 160 rpm for at least 5 h. Each phase was analyzed using Bellingham + Stanley Limited 60/70 Abbe Refractometer (No: A 92087) by the help of calibration lines obtained for each component in each layer.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

Liquid-liquid equilibrium (LLE) data for a ternary system of methyl eugenol (1) + linalool (2) + [EMIM][HSO₄] (3) were determined at 298.2 K (Figure 2). Othmer-Tobias correlation was used for the reliability of the experimental tie-line data. The immiscibility region was found using

distribution coefficients (D_i), separation factors (β) and selectivity (S) values. The solubility curves obtained by the cloud point titration showed that equilibrium of the ternary system was in Type II class in which two immiscible curve pairs were attained. Distribution coefficient, separation factor, selectivity were evaluated using immiscibility region. Obtained parameters show the extraction efficiency of the solvent. Distribution coefficient for the extracted component, separation factor and selectivity were calculated using the following expressions, respectively [25-27]:

$$D_i = \frac{w_{i2}}{w_{i1}}, \quad \beta = \frac{D_2}{D_1}, \quad S = \frac{w_{22}/(w_{22}+w_{12})}{w_{21}/(w_{21}+w_{11})} \quad (1)$$

where i in w_{ij} is the component of methyl eugenol (1), linalool (2), or IL (3) and j in w_{ij} is phase of raffinate(1) or extract (2).

Solubility data plotted to the triangular diagram shows that the ternary systems have Type II behavior since they present two immiscible pairs. Experimental liquid-liquid equilibrium values are consistent with a R^2 value of 0.896. Since the separation factors for linalool component are found to be less than 1 for binary methyl eugenol + linalool mixtures with a linalool composition lower than 0.45, [EMIM][HSO₄] is not selective for these linalool compositions. In case of initial linalool compositions higher than 0.45, the ionic liquid is selective for linalool since separation factor values are higher than 1. Selectivity of the ionic liquid increases with an increase of initial linalool composition and increasing trend becomes much higher. Separation factor also increases with an increase of linalool composition both in the extract and raffinate phases. However, the separation factor values are lower than 1 for linalool composition of 0.05 in the extract phase and 0.23 in the raffinate phase. After these linalool compositions, the values are higher than 1 with a higher increasing trend. Distribution coefficient (D_2), separation factor (β) and selectivity (S) values were given as a function of linalool fraction in the raffinate phase in Figure 3.

Despite lower distribution values, since separation factor is higher than 1 for the fraction values greater than 0.23 with an increasing trend, extraction can be possible. Separation factor values are also higher than 1 for the fraction values greater than 0.23 and increase from low concentration to high concentration of linalool changing from 0.53 to 5.18, meaning that the higher the concentration of linalool compounds in the feed, the higher the selectivity of [EMIM][HSO₄] to linalool. Low distribution coefficients and relatively higher separation

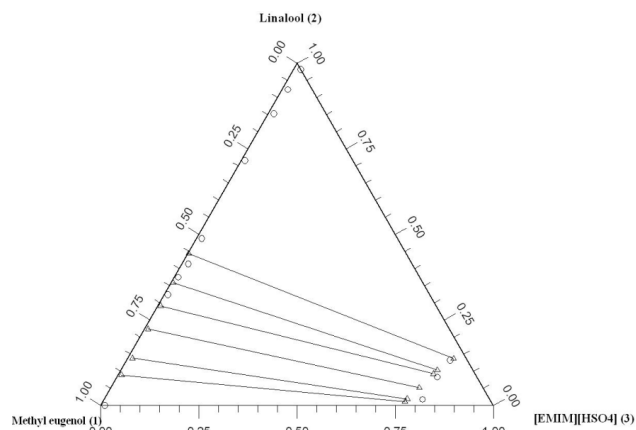


Figure 2: Ternary Diagram of {methyl eugenol (1) + linalool (2) + [EMIM][HSO₄] (3)} at 298.2 K: Experimental Solubility Curves and Tie-Lines.

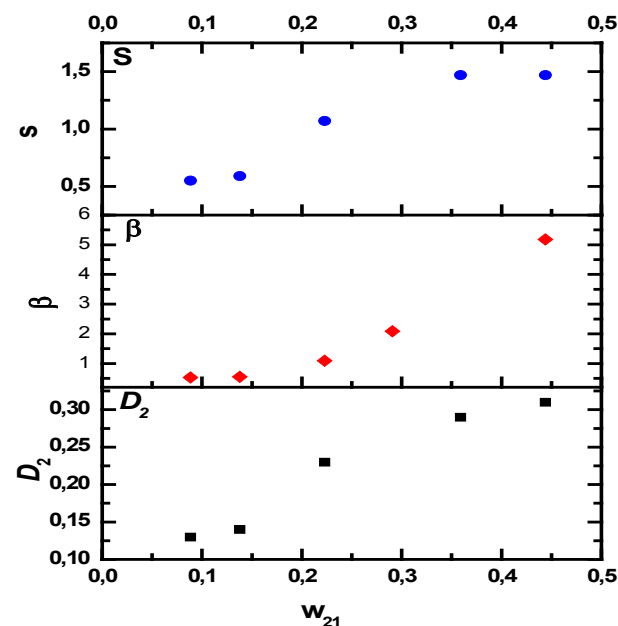


Figure 3: Distribution coefficient of linalool as a function of linalool fraction, separation factor as a function of linalool fraction and selectivity of ionic liquid as a function of linalool fraction in the raffinate phase.

factor values were also observed in literature for the separation of essential oil components by ILs, i.e., Arce et al. [9] calculated relatively lower distribution coefficients for limonene-linalool mixture extracted with 1-ethyl-3-methylimidazolium ethylsulfate with values 0.65 to 1.05 depending on the composition at 298.15 K. The values 0.53 to 1.03 were obtained at 318.15 K. As a comparison of distribution coefficient values of the experimental values with the ones in literature, distribution coefficient values

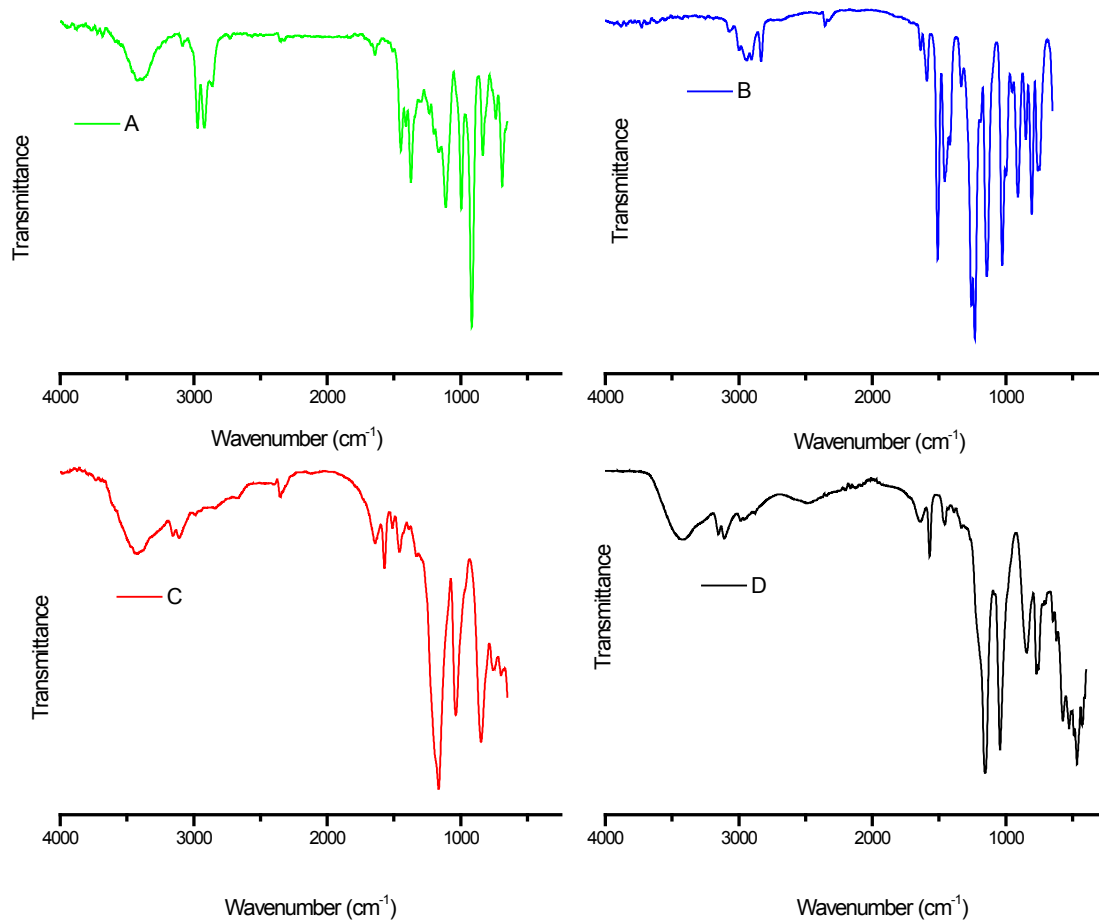


Figure 4: FTIR spectra of linalool (A), methyl eugenol (B), ionic liquid of [EMIM][HSO₄] (C) and the mixture of methyl eugenol-linalool-[EMIM][HSO₄] (D).

increase with an increase in linalool composition in raffinate and extract phases. However, while separation factor increases with an increase in linalool composition, the separation factor values in literature [9] decreases with an increase in linalool composition. Lago et al. [18] calculated relatively lower distribution coefficients for limonene-linalool mixture extracted with (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide with the values changing from 0.43 to 0.24 depending on the composition. In the case of separation values they calculated values changing from 8.97 to 2.20. In their study [18], both distribution coefficient and separation factor values decrease with an increase in linalool composition.

The structural characterization of methyl eugenol, linalool, [EMIM][HSO₄] (IL), and the ternary mixture in the homogeneous region (Meu (5%) + Lin (10%) + IL (85%)) was performed by FTIR and the spectra were presented in Figure 4. Characteristic peaks of [EMIM][HSO₄] observed at 1571/1461 and 1165 cm⁻¹ are attributed to skeletal vibration peaks of imidazole ring and bending vibration (in-plane)

of C-H from imidazole ring, respectively [28]. The bands assignable to the C-H stretching vibrations of the imidazole ring can be seen at 3155 and 3109 cm⁻¹ [28-30]. The bands at 1036 and 1165 cm⁻¹ are ascribed to symmetric -SO₃ [30, 31] and asymmetric [30] -SO₃ stretching vibrations, respectively. In the spectra, the characteristic fingerprint region for the fragrances such as methyl eugenol can be clearly observed between 700 and 1700 cm⁻¹ [32]. In the spectrum of Meu, the ring deformation and trans C-H (out-of-plane) are present at 805 and 953 cm⁻¹, respectively while the band at about 1630 cm⁻¹ can be attributed to the aromatic band [32]. The strong peak at 1026 cm⁻¹ is related to the trans C-H in phase wag, which is seen in FTIR of eugenol derivatives [32]. In the FTIR spectrum of linalool, peaks at 995, 1447, 2971 and 3422 cm⁻¹ are result of C-C, C-O, C-H, and O-H stretching vibrations, respectively [33].

In the spectrum of ternary mixture (Meu-Lin-IL), C-H stretching vibrations of the imidazole ring are present at 3152 and 3109 cm⁻¹ while O-H stretching vibration is observed at 3417 cm⁻¹. Some peaks in Meu (i.e. 1026, 953,

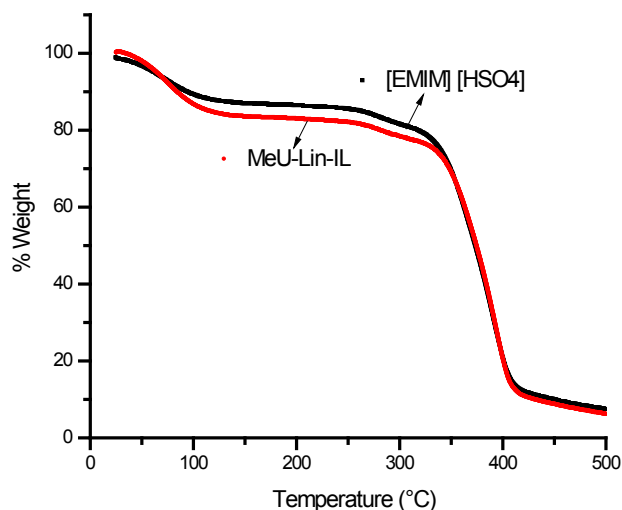


Figure 5: Thermogravimetric curves of $[EMIM][HSO_4]$ and Meu-Lin-IL.

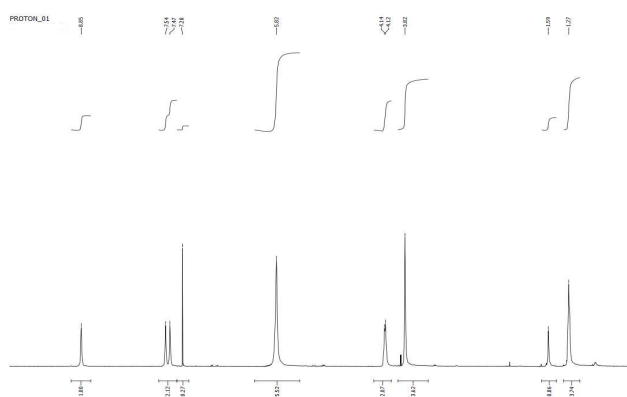


Figure 6: 1H -NMR spectrum of a ternary system (Meu-Lin-IL).

910 and 805 cm^{-1}) and linalool (i.e., 1373, 1112 and 995 cm^{-1}) disappeared in the spectrum of Meu-Lin-IL probably due to very low concentration of Meu and Lin in the ternary mixture. Two strong peaks of IL appear at 1036 and 1165 cm^{-1} shifted to 1042 and 1154 cm^{-1} in the spectrum of the mixture. The characteristic peak is still seen at 1571 cm^{-1} but the peak of IL at 1461 cm^{-1} shifted to lower wave number (1455 cm^{-1}).

The thermal behaviour of $[EMIM][HSO_4]$ (IL) and the ternary mixture in the homogeneous region (Meu (5%) + Lin (10%) + IL (85%)) was investigated by TGA and the corresponding thermograms are shown in Figure 5. Many ILs have high decomposition temperatures changing between 300 and 400°C [28]. It was stated that onset degradation temperature for $[Bmim][HSO_4]$ is 342.14°C [28]. Thermal decomposition temperature of $[EMIM][HSO_4]$ was given as 360°C [34]. In the current study, the weight losses of $[EMIM][HSO_4]$ are approximately 11, 13.5, 18, 30 and 79% at 100, 200,

300, 350 and 400°C , respectively. Weight loss became 92.5% at 500°C .

For purpose of comparison, thermal behaviour of the ternary mixture was analyzed. The TGA curve profiles of IL and Meu-Lin-IL are very similar (Figure 5). The weight losses of Meu-Lin-IL are found to be approximately 13, 17, 22, 31 and 80% at 100, 200, 300, 350 and 400°C , respectively. Weight loss became 94% at 500°C for this ternary mixture. It was reported that weight loss of linalool was 96.50% in the range of 30 – 150°C since it evaporates almost wholly at 200°C [33]. Because of the lower evaporating temperatures of linalool [33] and methyl eugenol [35] and their low concentration in the mixture, TGA curves reveal similar thermal behaviour of IL and (Meu-Lin-IL).

In general, 1H -NMR spectroscopy was used to determine the compositions of the components and to obtain LLE of the ternary systems [9, 18]. In the present study, characterization of the IL and ternary system was aimed. The sample of given composition (Meu (5%) + Lin (10%) + IL (85%)) within the homogeneous region was prepared. 1H -NMR measurement of $[EMIM][HSO_4]$ and (Meu-Lin-IL) was performed in $CDCl_3$ at 298 K and the spectrum of ternary system (Meu-Lin-IL) is presented in Figure 6. Some chemical shifts for $[EMIM][HSO_4]$ (figure is not given) can be listed as follows: 1.60 (t, 3H) [36,37], 3.77 (s, 3H) [30, 36, 37], 4.10 (2H) [30, 36, 37], 7.50 (s, 1H) [30, 36, 37] and 8.91 (s, 1H) [30, 36, 37]. In the spectrum of Meu-Lin-IL, the chemical shifts can be seen as 3.82 (3H), 4.12 (2H, $N-CH_2$) and 8.85 (1H, CH). In addition, the most evident difference is the appearance of a new peak (5.82 ppm) which can be assigned to presence of Lin and Meu.

4 Conclusion

The efficiency of the $[EMIM][HSO_4]$ to extract the linalool from the methyl eugenol + linalool mixture was probably firstly evaluated using the liquid-liquid equilibrium experimental data. Solubility data show that the behaviour of liquid-liquid equilibrium for (methyl eugenol + linalool + $[EMIM][HSO_4]$) (Meu-Lin-IL) system is in Type II class. Separation factor and selectivity of the ionic liquid increase with an increase in linalool composition of the initial binary mixture and in the extract and raffinate phases. However, ionic liquid is selective for an initial linalool compositions higher than 0.45 and after this value the increasing trend becomes much higher. Despite lower distribution values, since separation factor and selectivity parameters are higher than 1 for the linalool fraction values greater than 0.23 in the raffinate phase and 0.05 in

the extract phase, extraction can be possible. Selectivity and separation factor values show that the higher the concentration of linalool compounds in the feed, the higher the selectivity of [EMIM][HSO₄] to linalool. Thermal characterization of [EMIM][HSO₄] and (Meu-Lin-IL) system shows that both have substantially high thermal stability.

Conflict of interest: Authors declare no conflict of interest.

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