

Evaluation of Deep Eutectic Systems as an Alternative to Solvents in Painting Conservation

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Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 15451–15460

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ABSTRACT: Natural deep eutectic solvents (NADESs) are considered as green solvents, and due to their promising sustainability, they have been applied in many research fields. In this study, the main goal is to use various NADES systems to replace the traditional solvents used in conservation and restoration to remove varnish layers in a painting. The toxicity of traditional solvents, such as toluene or acetone, is well known in the chemistry field. To replace them, it is important to understand the intrinsic physicochemical properties of a solvent that may act as a substitute. Polarity and solubility are proposed as the best parameters required for this study. The Nile red probe was used to confirm the similarity between the polarity of deep eutectic systems (DESs) and traditional solvents. According to their polarities and Hansen solubility parameters, it is possible to predict the best solvents to solubilize the natural resin varnishes. Besides this, some arithmetic models can also be applied to estimate the critical or thermodynamic properties, which are useful tools to predict the behavior of these solvents. We have further proven the possibility of dissolving natural varnishes such as dammar or mastic in hydrophobic DESs, such as menthol + lauric acid, menthol + decanoic acid, or menthol + thymol.

KEYWORDS: painting, varnishes, NADES, group contribution, thermodynamic properties, Hansen solubility parameters, Teas chart



INTRODUCTION

Dammar and mastic are two examples of resins that originated from the trees of the family Dipterocarpaceae and plants of genus *Pistacia* of the family Anacardiaceae, respectively, and are the most studied varnishes.¹ The studies carried out since the 1960s about their properties such as composition, solubility, and aging time made them a model substance. Both have a low molecular weight, belong to the triterpenoid class composed of a ring system of 30 carbons (a cycle isoprenoid) and a complex mixture of oxidized functional groups that are present even when the resins are fresh and, in many cases, which are responsible for the presence of acidic functional groups in an aged resin. Also, the polymeric fraction of those resins improves the physical and optical properties by forming a coating layer over the paint film that protects and creates a uniform surface to work on.^{2–4} This layered structure often gives important information necessary for the removability/solubility tests, depending on the type of resin.

Deep eutectic systems (DESs), first described by Abbott in 2003,⁵ are currently one of the new fields of study of green technologies, besides ionic liquids (ILs). They are formed by a mixture of two or more organic compounds that are typically solid but can also be a liquid; at a particular molar ratio, it leads to a decrease of the melting point by the hydrogen bonding

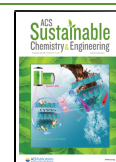
interaction and becomes liquid at room temperature.^{6–8} Natural deep eutectic solvents (NADESs) are formed when the compounds that constitute the DES are, principally, primary metabolites such as sugar, amino acids, and organic acids. Although the mechanism of DES/NADES formation is not yet well understood, these systems demonstrate that they fulfill most of the principles of green chemistry (e.g., low volatility and toxicity, biodegradability, biocompatibility, easy production, high purity, and so forth).^{9–14} The characterization of NADES involves the determination of their physicochemical properties such as polarity, viscosity, solubility, density, hydrophilicity, and freezing point,^{15,16} which are of extreme relevance to scaling up of the technology.

The main goal of this work is to use some of these systems to replace volatile organic solvents such as toluene, acetone, propanol, and so forth, commonly used in conservation and

Received: July 6, 2021

Revised: July 27, 2021

Published: November 11, 2021



restoration to remove varnish layers of natural resins such as mastic and dammar.

MATERIALS AND METHODS

DL-Menthol (Men) ($\geq 95\%$ purity, CAS: 89-78-1), borneol (Bor) (97.0%, CAS: 464-45-9), thymol (Thy) ($\geq 98.5\%$ purity, CAS: 89-83-8), myristic acid (Myr) ($\geq 98.0\%$ purity, CAS: 544-63-8), lactic acid (Lac) ($\geq 85.0\%$ purity, CAS: 50-21-5), lauric acid (Lau) ($\geq 98.0\%$ purity, CAS: 0143-07-07), betaine (Bet) ($\geq 99.0\%$ purity, CAS: 107-43-7), *iso*-octane ($\geq 99\%$ purity, CAS: 540-84-1), acetone ($\geq 95\%$ purity, CAS: 67-64-1), toluene (99.8% purity, CAS: 108-88-3), ethanol (96% purity, CAS: 64-17-5), methanol (99.8% purity, CAS: 67-56-1), *o*-xylene (97% purity, CAS: 95-47-6), 2-propanol ($\geq 95\%$ purity, CAS: 67-63-0), Nile red (98.0% purity, CAS: 7385-67-3), and decanoic acid (Dec) ($\geq 98\%$ purity, CAS: 334-48-5) were supplied by Sigma Aldrich. DL-Malic acid (Mal) (extra pure, CAS: 6915-15-7) was obtained from Scharlau. Shellsol A (CAS: 64742-95-6), Shellsol D40 (CAS: 64742-48-9), Shellsol T (CAS: 90622-57-4), turpentine (CAS: 8006-64-2), white spirit (CAS: 110-54-3), mastic (CAS: 61789-92-2), and dammar (CAS: 9000-16-2) were obtained from Kremer.

NADES Preparation. Different components were weighed and mixed with simultaneous stirring at 65 °C until a clear viscous liquid was formed. The preparation of DES was done according to Table 1.

Table 1. List of All the NADESs Studied and Their Visual Aspect Observed at Room Temperature

DES	visual aspect
Men + Lau (2:1) ¹²	transparent liquid
Men + Lau (4:1) ¹²	transparent liquid
Men + Lau (8:1) ¹²	white solid
Men + Myr (4:1)	white solid
Men + Myr (8:1)	white solid
Men + Dec (2:1)	transparent liquid
Men + Dec (7:2)	transparent liquid
Men + Dec (1:3)	white solid
Men + Mal (8:1)	white solid
Men + Thy (1:1) ¹⁷	transparent liquid
Men + Thy (2:1)	transparent liquid
Men + Thy (4:1)	transparent liquid
Men + Thy (8:1)	white solid
Men + Bor (7:2)	transparent liquid
Thy + Bor (1:1) ¹⁷	white solid
Lac + Bet + Dec (2:1:0.25)	white solid
Lac + Bet + Dec (2:1:0.35)	white solid
Lac + Bet + Dec (5:1:0.1)	white solid
Men + Lau + Dec (2:1:1)	transparent liquid
Men + Lau + Dec (4:1:1)	transparent liquid

Determination of the Water Content. The water content of all the systems was measured using the instrumental equipment 831 Karl Fischer coulometer with a generator electrode (Metrohm) and a moisture analyzer DAB (Kern).

Varnish Preparation. Both varnishes were prepared following the same process, that is, dissolving the resin gums in turpentine, in a ratio of 1:2 (w/v), while stirring at 35 °C. After preparing the varnishes, 10 glass slides were brushed with a thick coat of dammar, while another 10 glass slides were brushed with mastic varnish. The glass slides have 26 × 76 mm and were left to dry for a week at room temperature.

Determination of Physicochemical Properties. *Polarity.* The polarity of all the systems and solvents was determined with the solvatochromic method using Nile red, previously dissolved in ethanol, and then measured with a dilution of 1:200 of Nile red in a DES. This assay was performed in triplicate. The absorbance of the solutions was measured using a UV-visible spectroscopy (Thermo Scientific GENESYS 50 for the DES systems and Multimode plate

reader VICTOR NIVO for the traditional solvents) in the wavelength range of 400–800 nm.

Contact Angle. The measurement of the contact angle of NADESs was carried out using a KSV CAM-100 goniometer of KSV Instruments Ltd, configuring the number and interval of frames to, respectively, 60 and 1000 ms. The process consists of dropping a drop of solvent on the surface of the substrate and immediately starting data recording. Here, 24 glass slides varnished with dammar and mastic varnishes (12 for each) were used as the substrate, and each test was performed at least three times. The listed results correspond to the mean \pm standard deviation.

Viscosity and Density. Viscosity and density were determined using the Anton Paar equipment, model SVM 3001, an automated rotational Stabinger viscometer–densimeter. For all the systems, the range of the temperature scan selected was 20–60 °C. Each system was measured in triplicate, and the tabulated results shown represent their mean \pm standard deviation.

Estimation of Critical and Thermodynamic Properties. The precise models for estimating the thermodynamic properties of DES systems were made using the genetic programming. In the published models, the critical temperature (T_c), critical volume (V_c), and acentric factor (ω) are chosen as the input data for the equations proposed. Some equations showed in this work are simplified comparative to the original ones.¹⁸

RESULTS AND DISCUSSION

Polarity. The traditional varnishes, namely, dammar and mastic resin, are composed of polar (such as hydroxylic or carboxylic acids) or hydrophobic groups. Thus, DESs were selected according to the structural features of their components, which resulted in polarities similar to those of the traditional solvents or some of their mixtures used for varnish removal.

To evaluate the solvent's polarity, Nile red dye was chosen. Nile red has been used as a substantial lipophilic dye for fat stains; it exhibits large shifts at the wavelength of the maximum absorbance with solvent polarity and because of its unique stability in extremely acidic media and capacity to not lose molar absorptivity in the presence of acids as Reichardt's dye does, it has been used commonly as an alternative to Reichardt dye.^{19,20}

Using the same solvatochromic method, the interaction of probes/solvents can be measured by UV/visible spectroscopy.²¹ The solvatochromic absorption bands using Nile red were similar in all samples—a single typical spectral band around 400–600 nm with a wavelength corresponding to the maximum absorption.

The maximum wavelength (λ_{\max}) of each sample allowed the calculation of the polarity parameter (E_{NR}) using the following equation²²

$$E_{NR} = \frac{28,591}{\lambda_{\max}} \quad (1)$$

where the E_{NR} (kcal·mol⁻¹) is the energy of transition and λ_{\max} (nm) is the maximum wavelength of the Nile red dye dissolved in NADESs. Because the more polar solvents cause Nile red to be absorbed at higher wavelengths, according to eq 1, these solvents will have lower E_{NR} values. This shift in the λ_{\max} of Nile red by this type of solvent allows the calculation of the relative polarity of the solvent of interest.²³

The normalization for both (traditional solvents and NADESs) was made using the values from Table 2, considering water as the reference for the more polar solvent [E_{NR}^N (water) = 1.0] and *iso*-octane the reference for a more nonpolar solvent [E_{NR}^N (*iso*-octane) = 0.0], as shown below in

Table 2. Maximum Wavelength of Absorption, E_{NR} and Normalized E_{NR}^N Values of Traditional Solvents and Their Mixtures^a

solvents	λ_{max}	E_{NR}	E_{NR}^N	% water
water	585.32	48.85 ± 0.17	1.000	
Lac + Bet + Dec (5:1:0.1)	574.33	49.78 ± 0.05	0.903 ± 0.010	N/D
Thy + Bor (1:1)	562.33	50.84 ± 0.14	0.792 ± 0.010	N/D
Men + Thy (1:1)	561.67	50.90 ± 0.05	0.786 ± 0.010	0.157 ± 0.020
methanol	559.50	51.10 ± 0.05	0.765 ± 0.010	22,265 ± 0.210
Lac + Bet + Dec (2:1:0.35)	555.00	51.52 ± 0.09	0.722 ± 0.010	N/D
Men + Thy (2:1)	553.33	51.67 ± 0.11	0.706 ± 0.010	0.127 ± 0.020
Lac + Bet + Dec (2:1:0.25)	553.33	51.67 ± 0.22	0.706 ± 0.020	N/D
ethanol	552.33	51.76 ± 0.14	0.696 ± 0.010	<0.001
isopropanol	549.67	52.02 ± 0.07	0.670 ± 0.010	0.216 ± 0.020
Men + Thy (4:1)	549.00	52.08 ± 0.10	0.663 ± 0.010	0.133 ± 0.010
Men + Mal (8:1)	547.33	52.24 ± 0.11	0.646 ± 0.010	N/D
Men + Thy (8:1)	545.67	52.40 ± 0.06	0.630 ± 0.010	N/D
iso-octane/isopropanol (1:9)	542.00	52.75 ± 0.00	0.593 ± 0.010	0.513 ± 0.120
iso-octane/isopropanol (2:8)	541.67	52.78 ± 0.06	0.589 ± 0.010	N/D
iso-octane/isopropanol (3:7)	541.67	52.78 ± 0.06	0.589 ± 0.010	0.814 ± 0.090
Men + Bor (7:2)	540.33	52.91 ± 0.06	0.576 ± 0.010	0.158 ± 0.030
Men + Lau (4:1)	539.57	52.99 ± 0.07	0.568 ± 0.010	0.166 ± 0.020
acetone	539.50	53.00 ± 0.08	0.567 ± 0.010	<0.2
Men + Lau (8:1)	538.43	53.01 ± 0.07	0.556 ± 0.000	N/D
Men + Dec (2:1)	538.00	53.14 ± 0.00	0.552 ± 0.000	0.203 ± 0.020
Men + Myr (4:1)	537.67	53.18 ± 0.06	0.548 ± 0.010	N/D
iso-octane/iso-propanol (4:6)	537.33	53.21 ± 0.11	0.545 ± 0.010	0.459 ± 0.020
Men + Lau + Dec (4:1:1)	537.00	53.24 ± 0.01	0.542 ± 0.010	0.088 ± 0.010
Men + Dec (7:2)	536.67	53.28 ± 0.11	0.538 ± 0.010	0.140 ± 0.010
Men + Lau (2:1)	535.33	53.41 ± 0.06	0.524 ± 0.010	0.067 ± 0.010
Men + Lau + Dec (2:1:1)	535.00	53.44 ± 0.10	0.521 ± 0.010	0.144 ± 0.020
iso-octane/isopropanol (5:5)	535.00	53.44 ± 0.10	0.521 ± 0.010	0.465 ± 0.020
Men + Dec (1:3)	532.00	53.74 ± 0.00	0.489 ± 0.000	N/D
iso-octane/isopropanol (6:4)	530.67	53.88 ± 0.06	0.475 ± 0.010	0.494 ± 0.140
toluene	526.00	54.36 ± 0.00	0.425 ± 0.000	0.049 ± 0.000
iso-octane/isopropanol (7:3)	525.67	54.39 ± 0.06	0.422 ± 0.010	0.361 ± 0.210
Shellsol A	525.33	54.42 ± 0.06	0.418 ± 0.010	0.112 ± 0.000
xylene	524.67	54.49 ± 0.06	0.411 ± 0.010	0.110 ± 0.000
turpentine	518.67	55.09 ± 0.06	0.345 ± 0.010	N/D
iso-octane/isopropanol (8:2)	518.00	55.55 ± 0.06	0.300 ± 0.010	0.208 ± 0.190
white spirit (about 16% aromatic)	516.67	55.36 ± 0.03	0.323 ± 0.010	0.051 ± 0.000
iso-octane/isopropanol (9:1)	514.67	55.67 ± 0.06	0.300 ± 0.010	0.168 ± 0.020
Shellsol D40	494.50	57.82 ± 0.15	0.064 ± 0.020	0.008 ± 0.000
Shellsol T (0% aromatic)	494.00	57.88 ± 0.00	0.058 ± 0.000	0.008 ± 0.000
iso-octane	489.33	58.43 ± 0.03	0.000	0.006 ± 0.000

^aN/D—not determined.

eq 2. This normalization is based on the Reichardt method,²³ adapting the polarity extremes for the data set of this study.

$$E_{NR}^N = \frac{E_{NR}(\text{solvent}) - E_{NR}(\text{isooctane})}{E_{NR}(\text{water}) - E_{NR}(\text{isooctane})} \quad (2)$$

The traditional solvents used to remove varnish layers can be a pure solvent or a mixture of solvents. Mixing two organic compounds with different solubilities (e.g., aliphatic hydrocarbons with weak alcohols) may minimize the risk of swelling and impregnation in the lower layers of the painting.²⁴ Not only the polarity of systems but also there are more empirical features that are taken into consideration by the conservators to make the best decision on the solvent or combination of solvents to be used. The polarity of the traditional solvents used to remove varnish layers was determined following the same procedure used for NADESS, and the results are shown

in Table 2, with the polarity decreasing from the top to the bottom of the table.

Observing the polarity values presented above in Table 2, it is possible to compare and organize some of them by a similarity order. The graphic in Figure 1 shows that some organic solvents such as acetone, isopropanol, ethanol, iso-octane/isopropanol (5:5), and iso-octane/isopropanol (4:6), may be replaced with systems such as Men + Lau (4:1) or Men + Bor (7:2), Men + Thy (4:1), Men + Thy (2:1), Men + Lau + Dec (2:1:1), and Men + Lau + Dec (4:1:1) respectively, considering the polarity parameter (E_{NR}^N). This provides indications of which of the NADES systems could be used in the replacement of the conventional solvents if only polarity was to be considered.

Water contents of the solvents are also listed in Table 2. These values correspond to an average of at least three measurements. Because it may interfere with the polarity of the

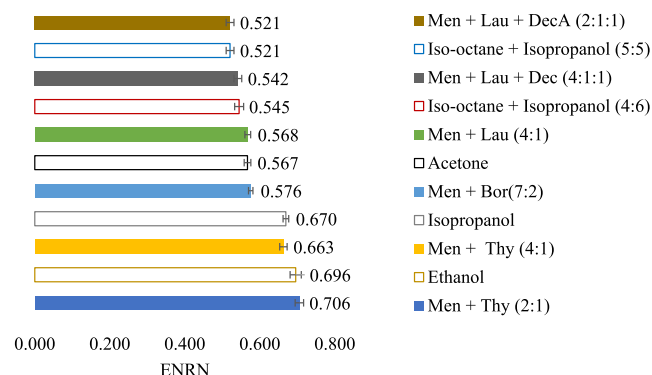


Figure 1. Polarity comparison between traditional solvents (colorless graphic bars) and some NADES systems. This graphic shows some solvents which can, possibly, be replaced by a specific NADES. For comparison, normalized values were used.

samples and become another important factor that needs to be considered, the water present in the systems was strictly controlled by Karl Fisher, and the risk is minimized.

The components of NADES in this study contain hydroxylic or carboxylic groups. These groups can facilitate the formation of hydrogen bonds and, hypothetically, when they are interacting, they may expel water molecules out of the system. For this reason, the percentage of water present is low (less than 0.3%) and the influence on the system's polarity is very limited.

Removability/Solubility Test. Through the polarity evolution it is possible to select some promising systems which can be used to test the ability of NADES to remove the varnish layer. The dry varnish on the glass blade surface was cleaned using a cotton swab containing the NADES. If successful, the glass will produce an effect such as the one shown in Figure 2.

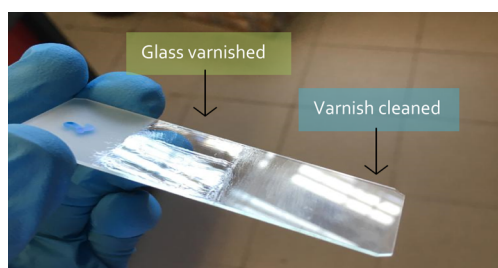


Figure 2. Glass slice containing dammar varnish, which was cleaned using the Men + Lau (4:1) system.

Figures 3 and 4 illustrate the investigated glass slides with mastic and dammar varnishes, after cleaning with different DESs, respectively. According to these figures, it is possible to successfully remove both varnishes with the selected eutectic systems. Glass slides with mastic varnishes 1–7 were cleaned using, respectively, with Men + Lau (4:1), Men + Lau + Dec (4:1:1), Men + Lau + Dec (2:1:1), Men + Thy (2:1), Men + Thy (4:1), Men + Bor (7:2), and Men + Dec (4:1). While glass slides with dammar varnishes 1–6 were cleaned using Men + Lau (4:1), Men + Lau + Dec (4:1:1), Men + Lau + Dec (2:1:1), Men + Thy (2:1), Men + Thy (4:1), and Men + bor (7:2), respectively.

The dammar resin has proved to be soluble at least in 1:2 (w/v) DESs—same proportion as it is solubilized in

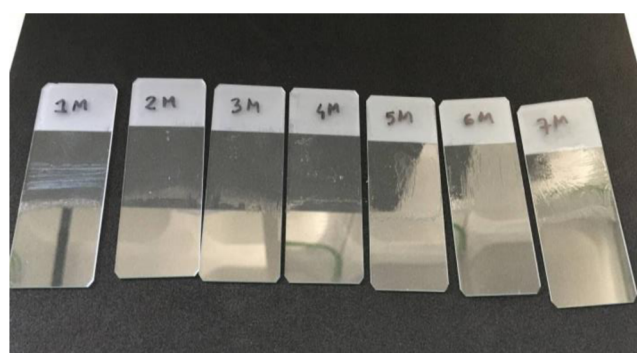


Figure 3. Glass slides with mastic varnish, after cleaning (the bottom half of the glass slide) with NADESs: (1) Men + Lau (4:1), (2) Men + Lau + Dec (4:1:1), (3) Men + Lau + Dec (2:1:1), (4) Men + Thy (2:1), (5) Men + Thy (4:1), (6) Men + Bor (7:2), and (7) Men + Dec (4:1).

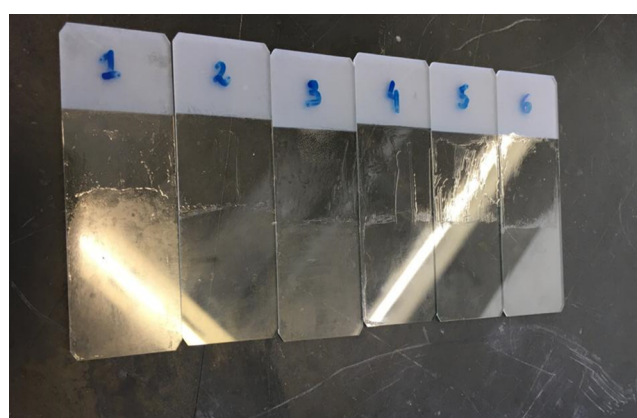


Figure 4. Glass slides with dammar varnish, after cleaning (the bottom half of the glass slide) with NADESs: 1. Men + Lau (4:1), 2. Men + Lau + Dec (4:1:1), 3. Men + Lau + Dec (2:1:1), 4. Men + Thy (2:1), 5. Men + Thy (4:1), and 6. Men + bor (7:2).

turpentine. To quantify the solubility degree of dammar, three different eutectic systems that are relatively less polar were selected (Figure 5), namely, Men + Dec (1:3), Men + Lau (2:1), and Men + Lau (4:1). It was observed that dissolving consecutively a certain amount of dammar resin in 3 mL of NADES, there is a maximum quantity until a glue coat is formed: 1.73, 1.5, and 1.53 g for 1, 2, and 3, respectively, as shown in Figure 5.

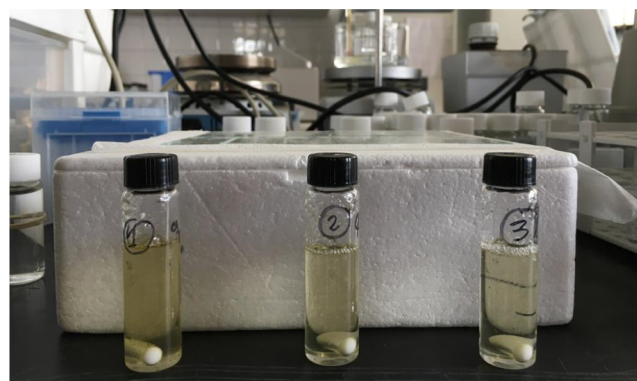
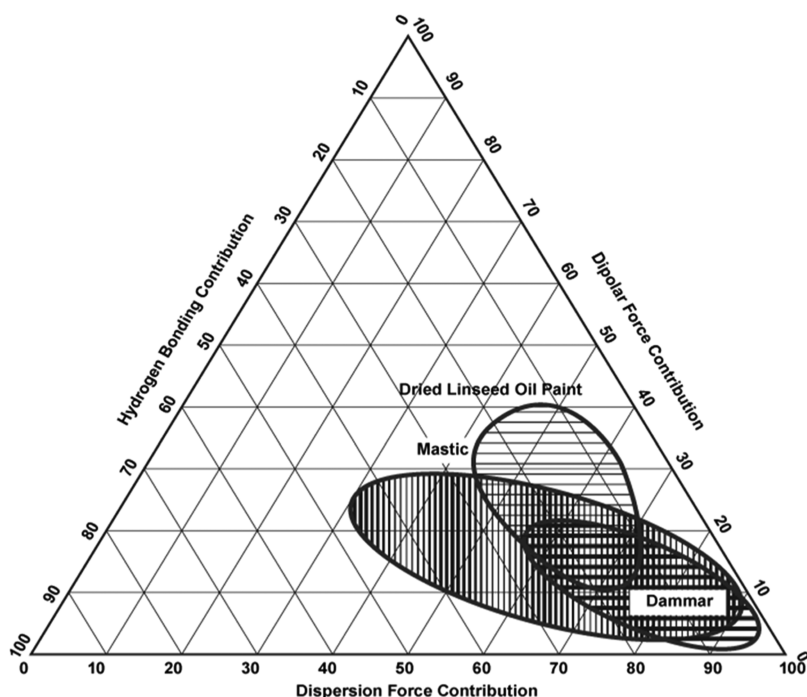


Figure 5. Dammar resin dissolved in different NADESs: (1) Men + Dec (1:3); (2) Men + Lau (2:1), and (3) Men + Lau (4:1).

Chart 1. Teas Plot for the Estimated Solubility of Mastic, Dammar, and Dried Linseed Oil Paint^a

^aRef: <https://www.naturalpigments.com/artist-materials/resin-mediums-damar-maroger/>.

Table 3. Hansen's and Hildebrand's Total Solubility Parameters of the Set Solvents with Similar Polarity Calculated (in MPa^{1/2}) Using Hoftzyer and Kreveleńs Method and Their Respective Fractional Solubility Parameters

solvents	δ_d	δ_p	δ_h	δ_t	F_d	F_p	F_h
Men + Lau + Dec (2:1:1)	17.0	2.4	8.6	19.2	61.7	8.5	30.8
iso-octane/isopropanol (5:5)	9.3	2.1	5.1	15.5	56.4	12.5	31.0
Men + Lau + Dec (4:1:1)	17.3	2.5	9.3	19.8	59.5	8.7	31.8
iso-octane/isopropanol (4:6)	10.1	2.1	5.1	16.2	51.9	13.8	34.2
Men + Lau (4:1)	17.6	2.6	9.7	20.2	58.8	8.7	32.4
acetone	15.3	10.4	5.2	19.2	49.5	33.7	16.9
Men + Bor (7:2)	18.5	2.9	10.8	21.6	57.3	9.1	33.6
isopropanol	14.8	6.5	16.2	22.9	39.4	17.4	43.1
Men + Thy (4:1)	18.0	2.9	10.8	21.2	56.8	9.2	34.0
ethanol	15.4	8.6	18.5	25.6	36.3	20.2	43.6
Men + Thy (2:1)	18.0	3.0	10.9	21.3	56.8	9.3	34.1

The same amount of mastic resin is dissolved in the systems as described above in Figure 5. However, the viscosity of the products that formed was relatively low; this is because although the solubility behavior of dammar appears to be similar to mastic, when fresh, its polymeric fraction makes this kind of resin not completely soluble in alcohol-based solvents, such as ethanol. On the other hand, mastic is slightly more polar than dammar.² These effects were observed during the cleaning process; while dammar-coated slides are more susceptible to solubilization with more hydrophobic systems, relatively more polar systems are able to better solubilize the mastic.

Teas Chart. A Teas chart is a useful tool often used by the conservators to locate the solubility region of various solvents. It is based on a triangular graphic that uses the three Hansen's solubility parameters (δ_d —dispersion forces; δ_p —polar forces; and δ_h —hydrogen bonding) to describe solvents power.²⁵ The mapped “solubility regions” of fresh dammar and mastic, presented in Chart 1, help select which NADESs are less likely

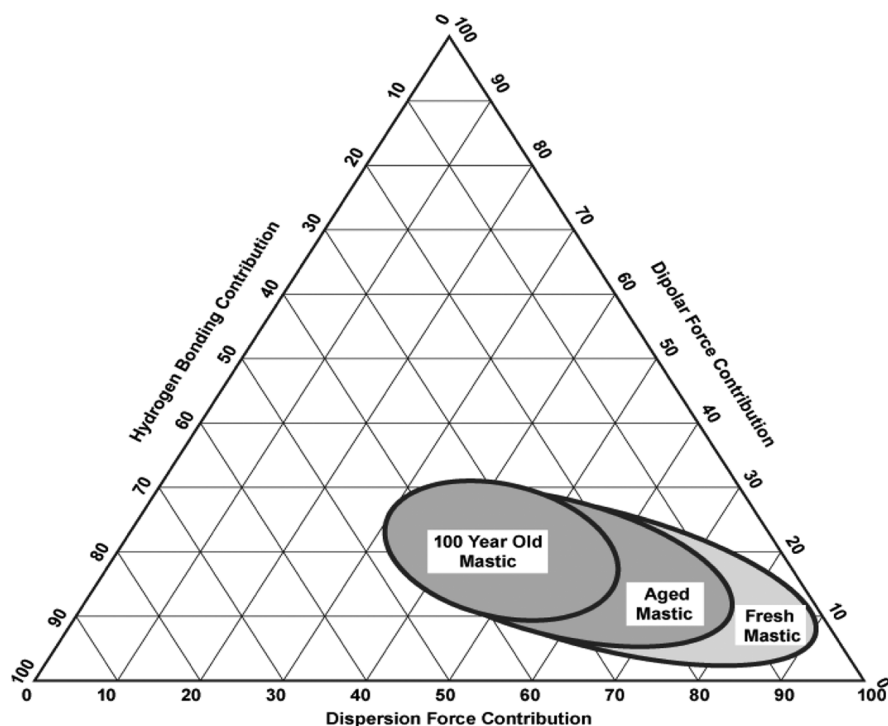
to damage the oil paint and then be used to remove the varnish.

Estimation of Solubility Parameters. Hansen's solubility parameters (δ_d , δ_p , and δ_h) of the most promising DES and traditional solvents listed in Table 2 were estimated using the group contribution method of Hoftzyer–Van Krevelen's²⁶ (see more in the Supporting Information). Once known, these parameters can be used to calculate the three fractional solubility parameters presented in eqs 3–5

$$F_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \times 100 \quad (3)$$

$$F_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \times 100 \quad (4)$$

$$F_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \times 100 \quad (5)$$

Chart 2. Teas Plot for the Estimated Change in the Solubility of Mastic as a Function of Light Aging^a

^aRef: <https://www.naturalpigments.com/artist-materials/resin-mediums-damar-maroger/>.

where F_d , F_p , and F_h correspond to the relative contributions to the cohesiveness of the substance of three types of intermolecular forces: dispersion, polar, and hydrogen bonding, respectively.²⁷ These parameters were calculated and are listed in Table 3. Here, DES and any other solvent with a similar polarity are presented in the same color. When locating the approximate position of each compound on the Teas plot in Chart 1, it is possible to observe that both DES and traditional solvents lie in the “solubility region” of mastic; however, with respect to dammar, the values, both for DES and traditional solvents, are outside of its region. Although this seems to contradict the experimental results presented in Figure 5, literature only gives us the position of a very small number of solvents because most of the solvents used to clean are hydrophobic or ternary mixtures of compounds such as acetone, diacetone, alcohol, and mineral spirits.^{27–29} In fact, dammar is considered better than mastic, as a picture varnish, due to its resistance to yellowing, optical qualities, and lower polarity.²⁸ Because hydrogen bonding is the predominate intermolecular force in the eutectic system formation, it is expected that there is a high contribution of F_h (and F_p) and, consequently, a low contribution to F_d . This means that the DES’s position can be oriented to the “solubility region” of dammar (more to the right of F_d), if its hydrophobic character increased. To solve this problem, regarding the more commonly used solvents, many authors proposed the use of binary mixtures, such as acetone/mineral spirits, propan-2-ol/butanone and propan-2-ol/iso-octane, progressively varying their proportions.^{4,25} Mixing solvents with different solubility behaviors has the advantage of allowing the adjustment or refinement of the solvent power and selecting which one can be used.

By analyzing the graph in Chart 1, it is also possible to observe that a solvent with values of F_d , F_p , and F_h in the

ranges of 60–70, 10–20, and 10–25, respectively, will solubilize any of those resins. However, the important issue here is the knowledge of the solubility region for the oil paint. If the oil paint is too sensitive to the solvent, upon contact, it can lead to softening, swelling, and consequent removal of the exposed pigments.⁴ Another tool often used to classify the swelling degree or miscibility of solvents is the Hildebrand total solubility parameter (δ_t).²⁶ It is based on Hansen’s solubility parameters (δ_d , δ_p , and δ_h , in $\text{MPa}^{1/2}$), which can be calculated using the following equation

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (6)$$

According to Stolor,^{24,30} an organic solvent will produce the greatest degrees of swelling, if its value of δ_t is in the range of 18–22.5 $\text{MPa}^{1/2}$. As can be seen in Table 3, the values of all the DESs are in this range. However, it is important to clarify that the Hildebrand parameter is not the best tool to describe the eutectic system behavior, due to the low accuracy regarding polar or hydrogen bonding solvents.^{31–33}

Aging Varnish. Aging is the main factor responsible for the change in varnish solubility, which is caused by many natural processes (e.g., photo-oxidation by the light influence). It leads to the increase of hydrophilic and acidity characters of the varnish and consequently the increase of strongly polar functional groups such as hydroxyls and carboxylic groups.^{3,34} It causes a significant increase of the values of F_h and F_p and decrease of the F_d values. In fact, Feller¹ points out that a value of F_d above 68 can lead to the swelling of the oil paint.²⁵ What is noticeable is that, once aged, the varnish will no longer be soluble in certain solvents previously used. In these cases, Teas chart parameters provide very relevant information for the possible mixtures that could be tested. As can be seen in Chart 2, solvents more polar are required during the aging process

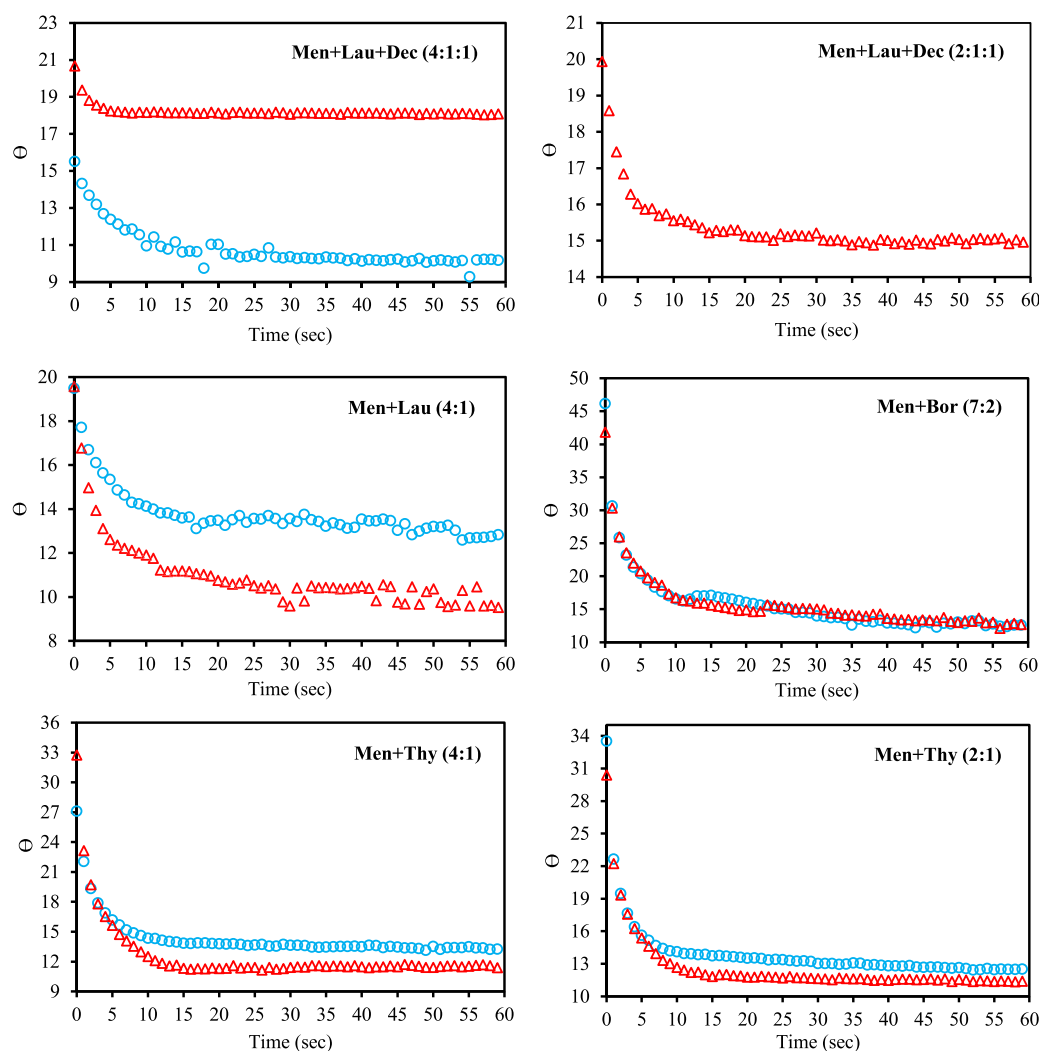


Figure 6. Measured contact angles of investigated NADESs on surfaces varnished with varnishes based on natural mastic and dammar resins (mastic O and dammar Δ).

Table 4. Measured Experimental Contact Angles, Polarities, and Viscosities of the Investigated NADESs in This Study

NADES	θ_{average}		E_{NR}^{N}	viscosity (mPa·s)
	mastic	dammar		at 293.15 K
Men + Lau + Dec (4:1:1)	10.79 ± 1.12	18.22 ± 0.37	0.542 ± 0.010	30.11 ± 0.07
Men + Lau + Dec (2:1:1)	not defined	15.39 ± 0.86	0.521 ± 0.010	23.24 ± 0.04
Men + Lau (4:1)	13.77 ± 1.20	11.01 ± 1.72	0.568 ± 0.010	42.50 ± 0.62
Men + Bor (7:2)	15.77 ± 5.20	15.90 ± 4.69	0.576 ± 0.010	150.69 ± 0.33
Men + Thy (4:1)	14.34 ± 2.25	12.61 ± 3.39	0.663 ± 0.010	79.69 ± 0.18
Men + Thy (2:1)	13.94 ± 3.06	12.68 ± 3.03	0.706 ± 0.010	68.94 ± 0.16

because it is well known that, once aged, the varnish often is no longer soluble in various solvents previously used.

Physical Properties: Contact Angle, Viscosity, and Density. Besides polarity, other important physical properties are also relevant to this study. Measuring the contact angle, it confirmed the solubilization of both types of varnishes by NADESs and traditional solvents; however, compared to traditional solvents, where the drop is rapidly absorbed upon contact with the surface of the varnishes, NADES drops are slowly absorbed by the varnish. On the other hand, by analyzing the presented behaviors in Figure 6, it is obvious that the contact angle of the six NADESs presented are very low ($<20^\circ$). This effect is commonly associated with a substrate

with a high surface energy, which more easily attracts the drop, leading to a good wetting.^{35,36} According to Fox–Zisman,³⁷ a low contact angle surface reveals a greater interaction between the drop and the investigated surface, comparative to the internal force of the drop. It may be a significant advantage for conservators because it allows them to have more control on the removability/solubility tests.

Another interesting observation regarding the contact angle that was presented by NADESs with the same components, but with different molar ratios [Men + Dec + Lau (2:1:1) and Men + Dec + Lau (4:1:1), as well as Men + Thy (4:1) and Men + Thy (2:1)], is that the less polar ($<E_{\text{NR}}^{\text{N}}$) system is more attracted by a dammar varnished surface. Also, regarding the

Table 5. Critical and Thermodynamic Properties of the Studied Solvents Using Correlative Models^a

solvents	M_w (g/mol)	T_c (K)	P_c (bar)	V_c (cm ³ /mL)	ω	ρ (g/cm ³)	C_p (J/mol·K)	σ (mN/m)
Men + Lau + Dec (2:1:1)	171.28	826.18	20.09	720.05	0.940	1.108	470.75	10.49
iso-octane/isopropanol (5:5)	87.16	537.22	34.01	326.5	0.420	0.954	172.91	31.2
Men + Lau + Dec (4:1:1)	166.28	688.65	22.95	637.38	0.796	1.112	378.42	10.48
iso-octane/isopropanol (4:6)	81.75	534.50	36.25	309.64	0.446	0.965	154.18	31.27
Men + Lau (4:1)	165.07	735.56	27.82	529.48	0.584	1.101	309.56	11.88
acetone	58.08 ^b	508.10 ^b	47.00 ^b	209.00 ^b	0.304 ^b	0.785 ^c	124.50 ^d	23.10 ^e
Men + Bor (7:2)	155.82	786.05	34.51	472.82	0.48	1.162	297.86	22.62
isopropanol	60.09 ^b	508.30 ^b	47.62 ^b	220.00 ^b	0.665 ^b	0.785 ^c	143.69 ^d	24.00 ^e
Men + Thy (4:1)	155.06	700.53	31.95	449.46	0.517	1.002	297.57	24.97
ethanol	46.06 ^b	513.92 ^b	61.48 ^b	167.00 ^b	0.649 ^b	0.789 ^c	114.90 ^d	21.82 ^e
Men + Thy (2:1)	154.25	687.98	32.87	428.18	0.523	1.098	296.52	27.97

^aThese parameters were estimated at 298.15 K. ^bCritical properties, ref 44. ^cDensity, ref 45. ^dHeat capacity, ref 46. ^eSurface tension, ref.: https://www.engineeringtoolbox.com/surface-tension-d_962.html.

angle stability on the surface of the dammar varnish, the NADES, Men + Lau + Dec (4:1:1) showed a good angle stability after 5 s; conversely, Men + Lau + Dec (2:1:1) showed angle stability after 15 s, and finally Men + Thy (4:1), Men + Thy (2:1), and Men + Bor (7:2) showed it after 10 s. On the other hand, with a mastic varnish as the substrate, Men + Dec + Lau (4:1:1) was shown to stabilize at 30 s, while Men + Thy (4:1), Men + Thy (2:1), and Men + Bor (7:2) stabilized after 10 s. The average angles of NADES on mastic and damar are presented in Table 4. It was not possible to measure the contact angle of the system Men + Lau + Dec (2:1:1) on mastic because this system, compared to the others, is quickly absorbed by the substrate. Also, in the case of Men + Lau (4:1), it is very difficult to confirm the real angle on both varnishes because, as it can be seen in Figure 6, there is a higher variability over time for this system.

Table 4 also includes the experimental data on the viscosity of the systems. Regarding the presented NADES viscosities, it can be observed that the three most viscous systems [Men + Bor (7:2), Men + Thy (4:1), and Men + Thy (2:1)] are also the three systems with the characteristic behaviors mentioned above. They show a similar contact angle on the two different investigated varnishes. However, for the Men + Lau (4:1) and Men + Lau + Dec (4:1:1) systems, there is a significant gap between the angles formed with the two investigated varnished surfaces. Also, in order to have a more comprehensive investigation on the physical properties of studied NADESs, their values of density and viscosity have been measured over a wide temperature range of 293.15–333.15 K and are presented in Tables S1 and S2 of the Supporting Information. The information of densities and viscosities for each NADES can be useful for choosing the most appropriate NADES according to the conditions and aims of each application. Because, in addition to the important properties of polarity and contact angle, density and especially viscosity should be considered as important operational properties for using NADES as new solvents. The interesting point of the measured densities of Table S2 is smaller density values with respect to water densities under the same conditions. Also, according to Table S1, two NADESs of Men + Lau + Dec (2:1:1) and Men + Lau + Dec (4:1:1) showed significantly lower viscosity values with respect to the other investigated NADESs.

Estimation of Other Physical Properties. The group contribution models were first used to estimate the thermodynamic behavior of mixtures containing ILs, as they cannot be experimentally determined because the degradation

process starts when the temperature approaches its normal boiling point.³⁸ Because the DES systems are, to some extent, similar to ILs, it is possible to apply the same group contribution models to the estimation of critical properties. DESs have been recently introduced; therefore, most of their thermodynamic properties are still unknown. Our group has studied and screened the properties of the NADESs listed in the literature in order to propose correlations to estimate the physical properties of the DESs with high accuracy, avoiding the need for complex and time-consuming experiments. These methods are, therefore, very useful, allowing the development of a correlation with the properties which are experimentally measured.³⁹ For that, with only the knowledge of the molecular structure and the molecular weight of a compound, it is possible to estimate the critical properties of a certain compound. The accuracy of the estimated properties was reported in the literature and tested using the densities of the liquids. This has often been used by some authors in the study of ILs.^{38,40} The evaluation of the critical and thermodynamic properties of NADESs and traditional solvents was carried out using the modified Lydersen–Joback–Reid group contribution^{41,42} and the Lee–Kesler mixing rules,³⁸ as proposed by Knapp et al.⁴³ and are listed in Table 5. Details of the calculations of characterization properties of the investigated NADESs are presented in the Supporting Information.

Properties such as density, heat capacity, and surface tension are specific for each compound and help to better characterize and describe them. Compared to many other systems tested in the literature, the values presented are in the same range (see more details in the Supporting Information). Although density is a basic physical property of any chemical compound, these data are still unavailable for DES. This problem also applies to the relative surface tension data. Because the cleaning method consists of applying the solvent onto the paint surface, it is crucial to know what the surface tension is, and depending on the value of surface tension, it is possible to predict the capacity of absorption of DESs for the paint layers. In fact, penetration is one of the big challenges, when thinking about DESs as alternative solvents, because they do not evaporate. However, the viscosity of a DES can be an advantage, as it allows for a certain working time before penetration. Regarding the calculated surface tension of NADESs listed in Table 5, we notice that they present relatively low values of surface tension when compared to the traditional solvents. Surface tension also depends on the nature of the varnish surface (hydrophilic or hydrophobic), and because multiple layers of varnish (from the

surface to the pictorial layer) can have different degrees of aging, this will affect the absorption of a DES. Theoretically, the older the layer the better it will be dissolved with a DES.

CONCLUSIONS

In order to replace the traditional solvents by the DES in the field of conservation and restoration, it is crucial to understand their physicochemical properties. Because of the complexity of NADES, there are many parameters which affect the solubility strength. Surely, polarity is just one of those parameters for NADES characterization, as it can reflect the solubility of compounds. In the study of solvents commonly used in conservation, the polarity parameter was a good tool, allowing the identification of some similar properties between the two systems. Some of these DESs were then used as solvents to dissolve natural resin varnishes, proving the higher dissolving capacity of these systems. In this study, it was observed that when fresh, dammar and mastic are soluble in a wide range of compounds. However, knowing that the solubility of these resins changes over time, more experiments should be done. Nevertheless, through the contribution groups, it is possible to predict the behavior of a DES in the Teas chart. The Teas chart complemented this study because it showed theoretically that DESs can be used to remove the mastic varnish, even when aged. Nevertheless, further studies should be carried out regarding the dammar varnish and its "solubility region". The empirical three-dimensional method, although with some inaccuracies, if interpreted too rigidly, has the advantage of allowing the observation of the effects of solvents as well as their mixtures and establish where it lies on the Teas plot. Further, it allows one to determine the solvents that clean satisfactorily and swell the oil paint the least. Furthermore, determination of properties such as density, surface tension, heat capacity, and critical properties may be essential for a better understanding of these solvents, as well their behavior under certain conditions. For future works, it is crucial to test the acidity and/or solubility of the aged resin varnish samples removed using some of these selected DES systems and understand their effectiveness as well as limitations when used in the context of cleaning the varnish of an oil painting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c04591>.

Experimental densities and viscosities of investigated NADESs, calculation steps for the characterization of NADESs, and detailed procedure for the calculation of solubility parameters (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work received funding from ERC-2016-CoG 725034 and was supported by the Associate Laboratory for Green Chemistry-LAQV, financed by national funds from FCT/MCTES (UIDB/50006/2020).

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