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PAPER

# Physicochemical properties of green solvents derived from biomass†

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Several thermophysical properties (density, refractive index, speed of sound, surface tension, dynamic viscosity, static permittivity and vapour pressure) of five compounds classified as green solvents derived from biomass (furfural, furfuryl alcohol, levulinic acid, ethyl levulinate, butyl levulinate) have been obtained from 278.15 K to 338.15 K. A comparative study has been carried out and information regarding molecular interactions and structure has been obtained.

## Introduction

Several chemical or physical processes such as separation, reaction rates, mass and energy transfer or crystallization can be performed in the gaseous, liquid or solid state. However, the vast majority of these processes are carried out in the liquid phase or in solution due to the advantages of using solvents. Solvents allow the formation of homogeneous dispersions, along with making the mass and energy transport processes easier. They also modify reactivity and allow for the deposition of solids. It is obvious that the use of solvents is fundamental to the chemical industry, as their advantages are so many and so great that it would be difficult to remove them from the industrial processes.

The use of traditional solvents in the chemical industry produces well-known environmental problems from the consumption of unsustainable raw materials which cause the emergence of harmful derived chemical compounds that can be released to the environment. For these reasons, it is fundamental that new chemical processes be proposed, based on the Green Chemistry principles of Anastas and Warner,[1] which minimise the environmental impact of industrial processes. These principles can be seen as a compulsory handbook for all scientists when preparing their experiments and designing new compounds or working procedures. One of the bases of green chemistry is the elimination or replacement of hazardous products and reagents, inefficient processes and unsustainable raw materials. For this reason, the research and use of so-called green solvents is increasing rapidly.

In relation to raw materials, a large amount of the resources come from fossil reserves such as coal, natural gas or petroleum. The main problems of using these fossil resources are that they are not renewable and their availability is diminishing rapidly. Solvents from sustainable sources including those from biomass, which are usually obtained by fermentation, enzymatic

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knowledge that there is about them. It is evident that accurate information on the green solvents in a wide range of pressures and temperatures is needed to carry out cost-effective and reliable process design in order to use these green compounds in any chemical process. It is essential to learn not only their physicochemical properties, in the above-mentioned broad range of experimental conditions, but also their molecular behaviour when interacting with other molecules which might be present in the medium. Properties such as the static permittivity and polarizability, solubility, transport properties like viscosity or diffusion, thermal behaviour, and volumetric, surface or critical behaviour of solvents, both in their pure state and when forming mixtures with other solvents or with solutes present in the medium, are fundamental.[3,6,7]

This paper forms part of a broader study in which new synthesis routes for drugs are investigated, paying special attention to the substitution of traditional solvents for green ones. In this paper, the first of a series, a comprehensive comparative thermophysical characterization of five green solvents derived from biomass has been obtained as the starting point of the study. In this case, we present several thermophysical properties (density, refractive index, speed of sound, surface tension, dynamic viscosity, static permittivity and vapour pressure) of the solvents in a wide range of temperatures from 278.15 K to 338.15 K. In future works we shall complete the characterization of the selected solvents and expose *PVT* behaviour as well other properties.

The selected solvents included are from the furfural family, furfural and furfuryl alcohol, and the levulinic acid family, levulinic acid, ethyl levulinate, butyl levulinate. As far as we know, there is no study for these solvents analogous to the present one; however, we have found some previous studies in which vapour pressures of furfural are shown[8] and another one related to the conformational and thermodynamic properties of gaseous levulinic acid.[9]

The use of carbohydrates as the basis of the production of all these chemicals makes them renewable products; furfural and related compounds can be obtained from hemicellulose sources through a breaking up procedure of the raw material and a posterior dehydration of the obtained pentoses. Analogously, from dehydration and hydrolysis of cellulose and hexoses, levulinic acid and related chemicals can be obtained. Furfural-based solvents are used in many applications; the most important of them is in the polymer industry. These solvents are used in the production of dark thermostatic resins resistant to bases, acids and other solvents. Furthermore, they are used as solvents for phenolic resins or pigments of low solubility. Other uses can be as flavouring agents, lubricants, adhesives and precursors for many chemicals.[10] On the other hand, it has been proven that levulinic acid-based solvents can be used in the manufacturing of synthetic fibres, pesticides, pharmaceuticals, plastics and rubber, or as an acidulant in food. Moreover, levulinic acid and its esters are used as plasticizers, odorous substances and solvents in polymers, textiles and coatings.[11,12] Nowadays, these solvents do not show potential health risks and that is the reason why they are being used in the food and pharmaceutical industry without any known official complaints. The ecotoxicity of these solvents is very low, and thus their environmental profile is adequate considering their level of biodegradation, so they are being used in industry as solvents and reaction media as green substitutes of traditional chemicals.

## Results

Experimental values of density, refractive index, speed of sound, surface tension, absolute viscosity, static permittivity and vapour pressure of the studied liquids together with calculated molar refraction and isentropic compressibility at the studied temperatures can be found in the ESI.†

We have found a linear dependence of the properties refractive index, speed of sound, surface tension, and static permittivity with temperature in the range of measurements under study.[13–15] These experimental data have been correlated with the following equation:

$$Y = AT + B \tag{1}$$

where $Y$ is the studied property and $A$ and $B$ are adjustable parameters. Relative root-mean square deviations have been calculated using the following equation:

$$\text{RMSDr (\%)} = 100\left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_i^{\text{exp}} - Y_i^{\text{cal}}}{Y_i^{\text{exp}}}\right)^2\right)^{1/2} \tag{2}$$

where $n$ is the number of experimental data.

The best linear fitting parameters and relative root-mean square deviations between experimental and correlated values are presented in Table 1.

Density–temperature dependence is shown in Fig. 1. The results indicate that density decreases linearly with temperature. This property has been fitted with a modified version of the Rackett equation for saturation densities[16,17] instead of a linear equation in order to describe the volumetric behaviour of these compounds accurately:

$$\rho = \frac{A}{B^{[1+(1-T/C)D]}} \tag{3}$$

$A$, $B$, $C$ and $D$ being fitting parameters. The best adjustable parameters and relative root-mean square deviations are shown in Table 1. The values obtained for furfural, furfuryl alcohol and levulinic acid are higher than unity, while the experimental values obtained for the studied esters are smaller. Thermal expansion, $\alpha$, defined as $\alpha = (1/V_m)(\partial V_m/\partial T)$, with the molar volume being $V_m$, has been determined from experimental data. Values of $\alpha$ increase slightly with temperature, being quite similar for ethyl levulinate, butyl levulinate and furfural and somewhat smaller for furfuryl alcohol and levulinic acid. Calculated values at 313.15 K for the studied compounds are given in Table 2.

As shown in Fig. 2, the refractive index decreases with temperature. Higher values are obtained for furfural and furfuryl alcohol. Compounds coming from levulinic acid show smaller values of refractive indices.

The molar refraction, $R_m$, of the studied liquids has been calculated from experimental data of density and refractive index by using the Lorentz–Lorenz relation, $R_m = V_m[(n^2_D - 1)/(n^2_D + 2)]$ (Fig. 3). Calculated values can be also found in the ESI.† Molar refraction is considered the hard core volume of a mole of molecules; therefore, the free molar volume (unoccupied part of the molar volume)[14] can be derived easily. Free volume is

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**Table 1** Fitting parameters and relative root-mean square deviations for the measured properties of the studied green solvents

| Compound | Property | *A* | *B* | *C* | *D* | *RMSDr* (%) |
|---|---|---|---|---|---|---|
| Furfural | $\rho$/g cm$^{-3}$ | 296.32 | 0.450031 | 637.09213 | 0.555875 | 0.04 |
| | $n_D$ | −0.00052312 | 1.679513 | | | 0.00 |
| | $u$/m s$^{-1}$ | −3.6087 | 2516.48 | | | 0.03 |
| | $\eta$/mPa s | 0.0732 | 528.05 | 122.55 | | 0.08 |
| | $\sigma$/mN m$^{-1}$ | −0.1319 | 82.37 | | | 0.11 |
| | $\varepsilon$ | −0.26256 | 120.160 | | | 0.15 |
| | $p$/kPa | 6.175 | 1471.166 | 193.342 | | 0.84 |
| Furfuryl alcohol | $\rho$/g cm$^{-3}$ | 723.91 | 0.719769 | 412.92686 | 0.808908 | 0.01 |
| | $n_D$ | −0.00042575 | 1.612900 | | | 0.00 |
| | $u$/m s$^{-1}$ | −3.2066 | 2406.34 | | | 0.03 |
| | $\eta$/mPa s | 0.0321 | 762.2 | 147.44 | | 0.15 |
| | $\sigma$/mN m$^{-1}$ | −0.0999 | 68.82 | | | 0.12 |
| | $\varepsilon$ | −0.12490 | 54.243 | | | 0.45 |
| | $p$/kPa | 7.680 | 2253.345 | 233.58 | | 0.89 |
| Levulinic acid | $\rho$/g cm$^{-3}$ | 295.29 | 0.458763 | 827.65771 | 0.708365 | 0.03 |
| | $n_D$ | −0.0003426 | 1.541820 | | | 0.00 |
| | $u$/m s$^{-1}$ | −3.0135 | 2378.52 | | | 0.01 |
| | $\eta$/mPa s | 0.1048 | 610.611 | 189.88 | | 0.07 |
| | $\sigma$/mN m$^{-1}$ | −0.0993 | 72.12 | | | 0.11 |
| | $\varepsilon$ | −0.04344 | 32.056 | | | 0.06 |
| | $p$/kPa | 8.665 | 3585.420 | 293.474 | | 0.85 |
| Ethyl levulinate | $\rho$/g cm$^{-3}$ | 575.14 | 0.662346 | 430.36441 | 0.863809 | 0.01 |
| | $n_D$ | −0.00042815 | 1.547312 | | | 0.00 |
| | $u$/m s$^{-1}$ | −3.7208 | 2461.28 | | | 0.06 |
| | $\eta$/mPa s | 0.0625 | 568.30 | 132.49 | | 0.13 |
| | $\sigma$/mN m$^{-1}$ | −0.1045 | 63.87 | | | 0.12 |
| | $\varepsilon$ | −0.05480 | 29.164 | | | 0.14 |
| | $p$/kPa | 6.426 | 1643.191 | 175.463 | | 0.87 |
| Butyl levulinate | $\rho$/g cm$^{-3}$ | 285.28 | 0.471164 | 655.97326 | 0.652184 | 0.01 |
| | $n_D$ | −0.00041421 | 1.549802 | | | 0.00 |
| | $u$/m s$^{-1}$ | −3.5450 | 2398.92 | | | 0.06 |
| | $\eta$/mPa s | 0.0741 | 549.24 | 142.65 | | 0.05 |
| | $\sigma$/mN m$^{-1}$ | −0.0902 | 57.83 | | | 0.10 |
| | $\varepsilon$ | −0.03757 | 21.553 | | | 0.13 |
| | $p$/kPa | 6.002 | 1603.570 | 164.907 | | 0.87 |

**Table 2** Calculated properties for the studied green solvents; coefficient of thermal expansion, entropy of surface formation, dipole moment at 313.15 K, enthalpy of vaporization at 373.15 K and log *P*, making use of the AGLOPS method

| Compound | $\alpha$/kK$^{-1}$ | $\Delta S_\sigma$/mN m$^{-1}$ | $\mu$/D | $\Delta H_{vap}$/kJ mol$^{-1}$ | log *P* |
|---|---|---|---|---|---|
| Furfural | 0.9407 | 0.13 | 8.30 | 45.577 | 0.43 |
| Furfuryl alcohol | 0.8450 | 0.10 | 5.32 | 54.030 | 0.25 |
| Levulinic acid | 0.7661 | 0.10 | 6.08 | 64.199 | −0.14 |
| Ethyl levulinate | 0.9871 | 0.10 | 5.19 | 57.528 | 0.38 |
| Butyl levulinate | 0.9376 | 0.09 | 4.68 | 60.880 | 1.36 |

considered an important property for any solvent because it is strongly related to properties such as solute solvation or gas solubility.[3] The results indicate that esters butyl levulinate and ethyl levulinate are the studied compounds with the highest molar refraction values, followed by levulinic acid. Furfural and furfuryl alcohol show lower molar refraction values than those of the rest of the studied compounds. The calculated free volume associated to molar refraction shows important values for the studied esters. However, the relationship free volume/molar volume is about 0.75 for all the chemicals except for furfuryl alcohol, with a somewhat smaller relationship free volume/molar volume of 0.70.

Speeds of sound results are shown in Fig. 4. The values decrease with temperature, being smaller for esters ethyl levulinate and butyl levulinate and moderately higher for the rest of the studied compounds. From speed of sound and density experimental values, isoentropic compressibility (Fig. 5) has been determined thorough the Newton–Laplace equation. Calculated values of isoentropic compressibility for the chemicals in the range of temperatures studied can be found in the ESI.† The results indicate that isoentropic compressibilities are quite similar for furfural, furfuryl alcohol and ethyl levulinate, while for butyl levulinate and ethyl levulinate, the values are considerably higher. Isoentropic compressibility is related to the internal organization of the molecules, so that higher values for this property indicate a poorly packed structure.

The principle of independent surface action,[18,19] originally formulated by Langmuir, has often been used to describe the nanoscopic structure of a liquid surface. According to this principle, each molecule can act and interact independently of other parts of the same molecule; *i.e.*, each part of a molecule possesses a local surface free energy, and therefore the measured surface tension should correspond to the part of the molecule that is actually present at the interface. In this case, the temperature dependence of surface tension of studied chemicals can be found in Fig. 6. As expected, surface tension values decrease with temperature. It is noticeable that measurements for levulinic acid could not be performed under 290.65 K due to its melting point. Higher values of surface tension are found for furfural, followed by levulinic acid and furfuryl alcohol. Lower values are found for the esters, ethyl

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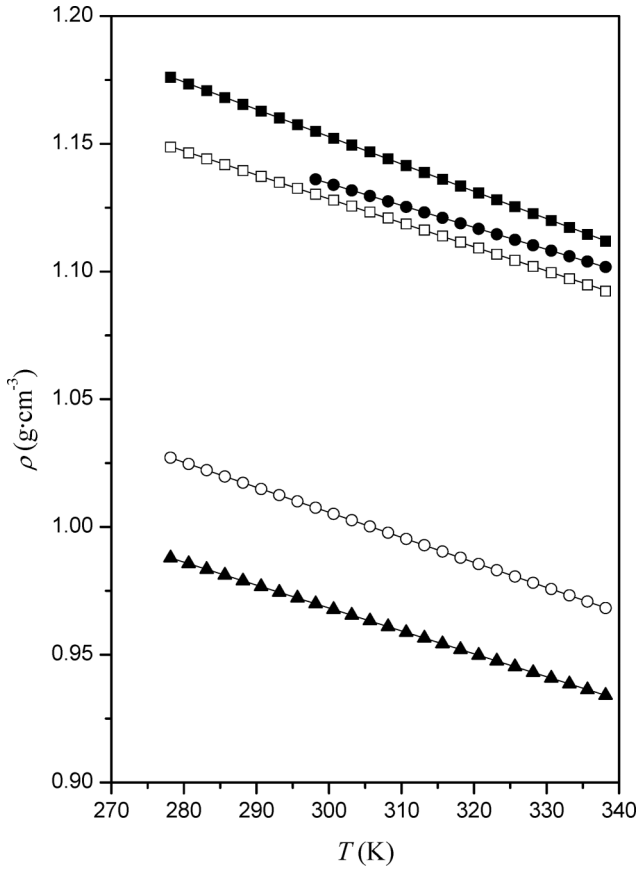


**Fig. 1** Density as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) Rackkett's equation.

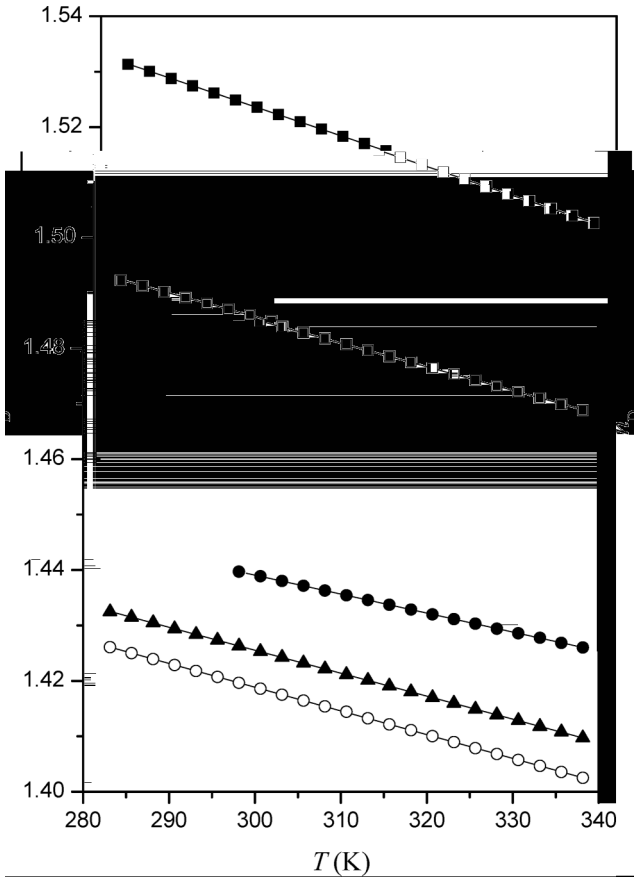


**Fig. 2** Refractive index as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) eqn (1).

levulinate and butyl levulinate. Furthermore, it has been pointed out that low values of entropy and enthalpy of surface formation leads to an enhancement of the orientation degree of molecules into the surface.[20] In order to achieve this information from experimental surface tension experimental data, the entropy ($\Delta S_\sigma = -(\partial\sigma/\partial T)_P$) and enthalpy ($\Delta H_\sigma = \sigma - T(\partial\sigma/\partial T)_P$) of surface formation per unit surface area has been determined. In this case, surface tension experimental values vary linearly with temperature. Consequently, the entropy of surface formation per unit surface area is in this range regardless of the temperature and the calculated values are shown in Table 2. The temperature dependence of enthalpy of surface formation per unit surface area is shown in Fig. 7; the values are shown in Table 7 of the ESI† and they decrease with temperature, the most marked tendency being the case of furfural.

Viscosity is a particularly interesting property for industrial applications, as large solvent volumes have to be stirred and pumped from several points of the factory to other ones. Furthermore, as we have mentioned before, interesting molecular information can be obtained from the analysis of this property. In Fig. 8, experimental results obtained for dynamic viscosity are shown. The temperature dependence is convex-curved type; therefore, experimental data have been fitted to the Vogel–Fulcher–Tamman equation:[20–22]

$$\eta = A\exp[B/(T - C)] \tag{4}$$

where $A$, $B$ and $C$ are adjustable parameters given together with the corresponding relative root-mean square deviations in Table 1. The experimental data show that levulinic acid and furfuryl alcohol are the ones with higher values of dynamic viscosity, followed by the esters and finally, furfural. However, surprisingly the dynamic viscosity values for levulinic acid are much higher than for the rest of the chemicals; therefore, it shows an important resistance to flow.

Experimental data of the static permittivities are gathered in the ESI† and shown in Fig. 9. Higher values of static permittivity are found for furfural, followed by levulinic acid and furfuryl alcohol. Lower values are found for the esters, ethyl levulinate and butyl levulinate. From the experimental data, the dipolar moment at 313.15 K has been calculated through the Onsager equation:

$$\mu^2 = \frac{9kTM}{4\pi N_A\rho}\frac{(\varepsilon - n_D^2)(2\varepsilon + n_D^2)}{\varepsilon(n_D^2+2)^2} = 1.642.10^{-4}\frac{4TM}{\rho}\frac{(\varepsilon - n_D^2)(2\varepsilon + n_D^2)}{\varepsilon(n_D^2+2)^2} \tag{5}$$

The values of the dipolar moment are shown in Table 2. The highest values have been found for furfural, while the ester butyl levulinate shows the lowest value of dipole moment.

The vapour pressure of the studied solvents has also been obtained experimentally. The esults have been correlated with the Antoine equation:

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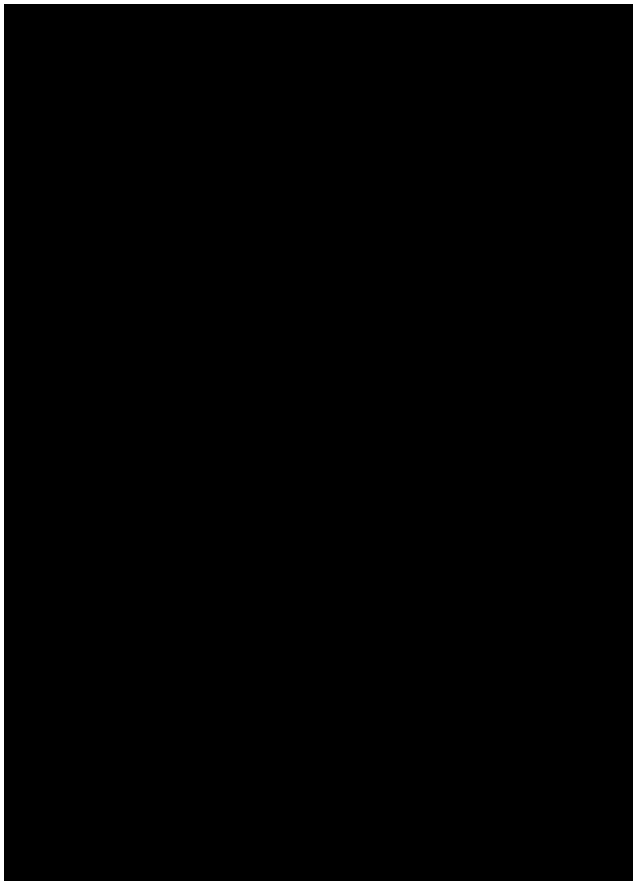

**Fig. 3** Molar refraction as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) correlation line.

$$\log p = A - \frac{B}{C + t} \tag{6}$$

where $t$ is temperature in degrees Celsius and $A$, $B$ and $C$ are adjustable parameters. Experimental data are represented in Fig. 10 and correlation values are gathered in Table 1. The experimental values can be found in the ESI.† Higher values of vapour pressure have been found for furfural family solvents followed by ethyl levulinate, butyl levulinate and levulinic acid. From the slope of the vapour pressure curve, the enthalpy of vaporization can be determined, through the Clausius–Clapeyron equation. Values for this property at 373.15 K are given in Table 2.

## Discussion

Analysis of a complete set of thermophysical properties, volumetric, spectroscopic, superficial or transport properties, is a common way to extract the molecular behaviour of chemical compounds regardless of their nature.[23–25] The molecular effects that characterize the compound can be displayed with different intensity depending on the studied property. In the case of volumetric properties such as density, speed of sound or refractive index, a general idea of the structural organization of the molecules in the liquid state can be achieved.[26–28] On the other hand, information about bulk interactions can be obtained

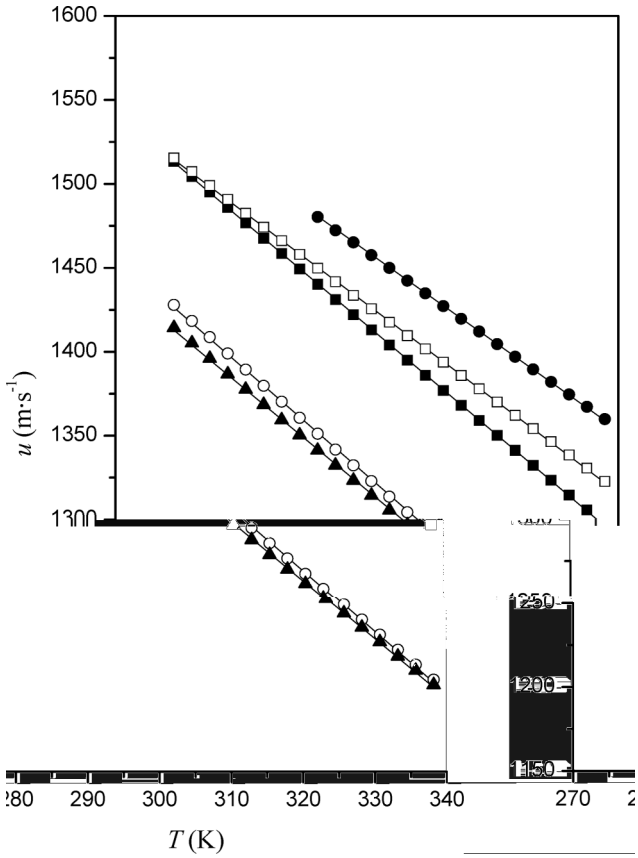


**Fig. 4** Speed of sound as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) eqn (1).

from properties like melting and boiling points, viscosity or surface tension. In relation to surface tension, it is obvious that information regarding molecular orientation on the surface can be also achieved, while viscosity not only depends on the interactions but is also a reflection of the internal organization of the molecules and their ability to flow.[29,30] Furthermore, considering a solvent as a nonstructured continuum, properties such as relative permittivity, dipole moments and refractive indices can be used as macroscopic physical parameters to characterize solvent polarity[5] In addition, solvent polarity parameters have demonstrated their ability not only to classify organic solvents but also to explain solvent effects on very different physical and chemical processes.[31]

Taking into account all the information obtained from the studied properties described earlier, we can obtain some information on the internal organization of the compounds and packing of molecules. The available free volume can be related to several molecular factors such as steric and structural effects, the magnitude of hydrogen bonding and some other intermolecular interactions and the dynamics of these interactions.[4] On the other hand, experimental results indicate that all of the studied chemicals can establish polar interactions between their molecules to a certain extent; static permittivities and dipole moments obtained from the studied compounds are relatively high, especially for furfural. In relation to the hydrogen bonding interactions that can be established between molecules, furfuryl alcohol and levulinic acid can develop hydrogen bonds

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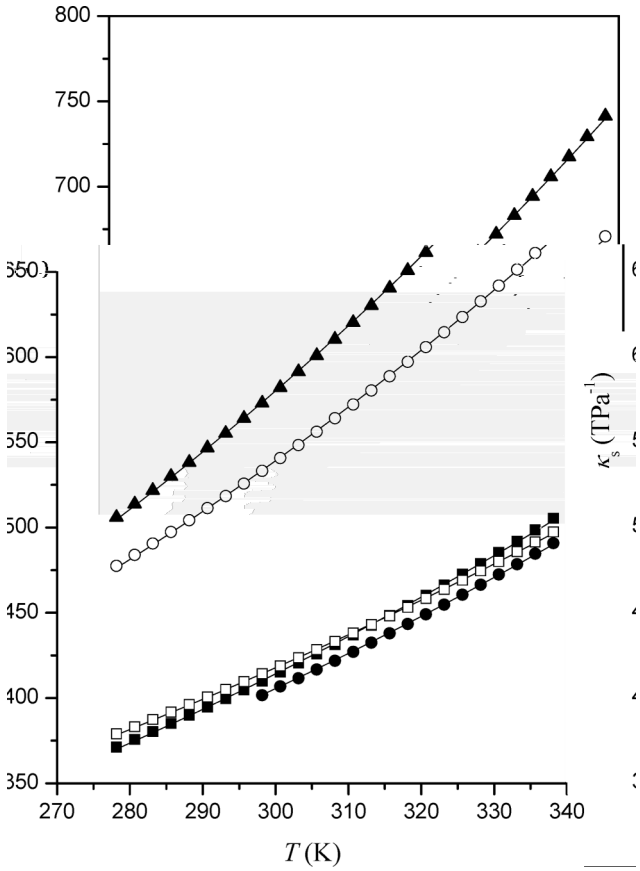


**Fig. 5** Isentropic compressibility as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) correlation curve.

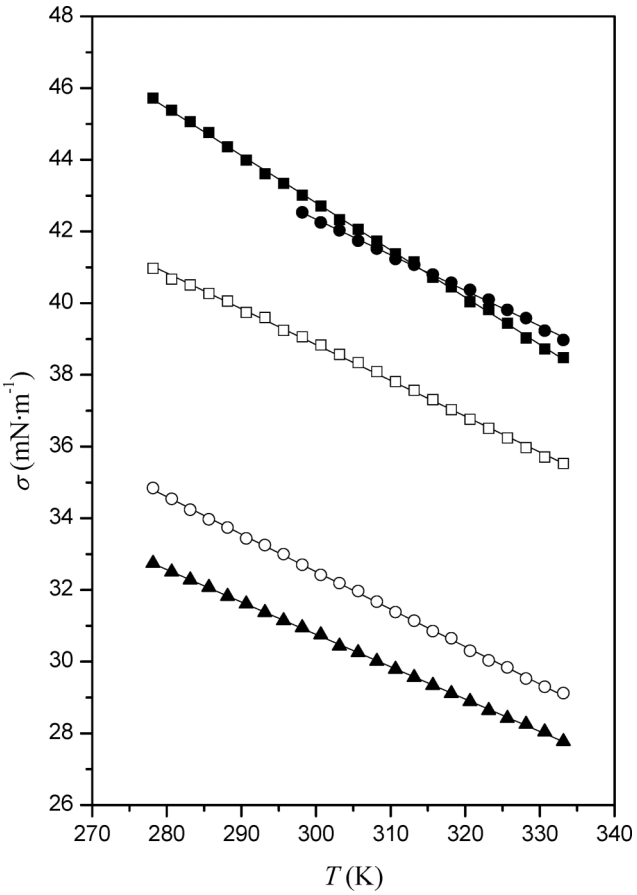


**Fig. 6** Surface tension as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) eqn (1).

thorough hydroxyl groups and alkoxy oxygens, while furfural and the esters are acceptors of hydrogen atoms. However, as Reichardt pointed out in his excellent review,[32] to achieve an idea of solvent polarity, one has to take into account not only macroscopic solvent parameters such as relative permittivities or dipole moments, but also the action of all, specific and nonspecific, intermolecular interactions.

Considering that the isoentropic compressibility values for the compounds coming from furfural are quite similar, we have to pay special attention to the free volume/molar volume relation, which was found to be lower for furfuryl alcohol, meaning a more packed structure than the rest of the chemicals. This could be due, on one hand, to an important amount of intermolecular interactions (hydrogen bonding interactions mainly), but above all to a better accommodation of the molecules due to the structure formed by the cyclic ether and a small alcohol group. It is also worth noting that the high free volume values found for butyl levulinate and ethyl levulinate correspond to a more compressible structure, probably due to the steric impediment in the internal organization of the molecules. The free volume of levulinic acid can be explained if we take into account two different factors that operate in opposite directions; important intermolecular interactions established between its molecules and steric impediment (similar to that observed for the studied esters). The counterbalance of these two opposite effects makes values of the molar free volume/molar volume similar to those obtained for the esters, in which, although polar interactions can be considered similar in extent, hydrogen bond interactions can not be established.

The study of the vapour pressures gives us important information related to the VOC character. It is known that one of the main problems connected to the use of organic solvents is the presence of these compounds in the atmosphere. The most common volatile organic compounds (VOCs) are frequently solvents such as chloroform or toluene. All the studied compounds from biomass present low vapour pressures; therefore, they can be considered as suitable candidates for substitution of VOCs. The low values of vapour pressures of levulinic acid must also be highlighted. Vapour pressure experimental data are also related to the amount of intermolecular interactions. In this case one has to take into account all types of interactions, specific and nonspecific, including those related to the surface area of the molecules (dispersive interactions). In this case, it is evident that intermolecular interactions between molecules of levulinic acid should be stronger than for the rest of the studied chemicals, being weaker for the chemicals coming from furfural, probably due to their noticeably smaller surface area.

To achieve an impression of molecular hydrophobicity, we have calculated the log $P$ (logarithm of 1-octanol/water partition coefficient) by using the AGLOPs method.[33–35] AGLOPS values found for studied compounds are given in Table 2. This parameter is closely related to miscibility with water, which is

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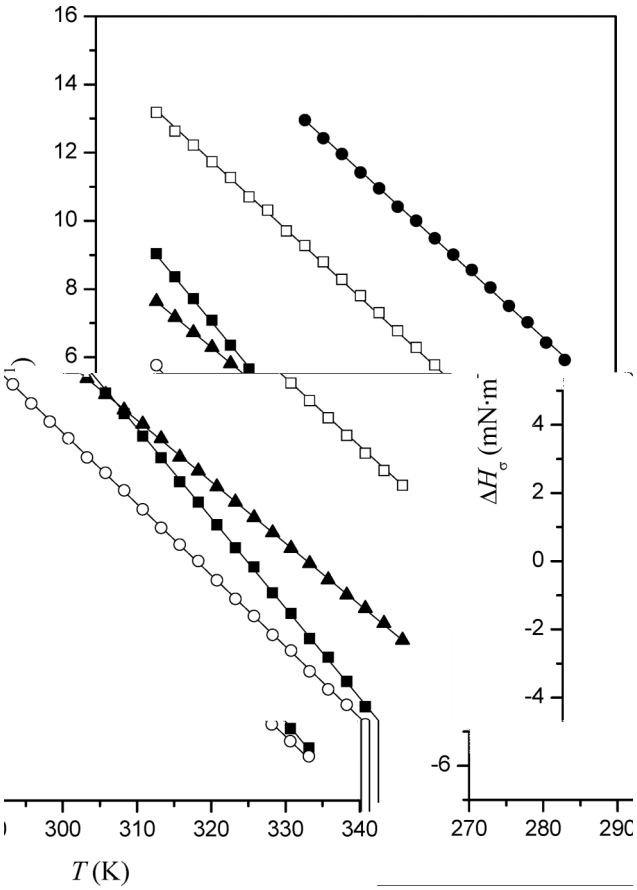


**Fig. 7** Enthalpy of surface formation per unit area as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) correlation curve.

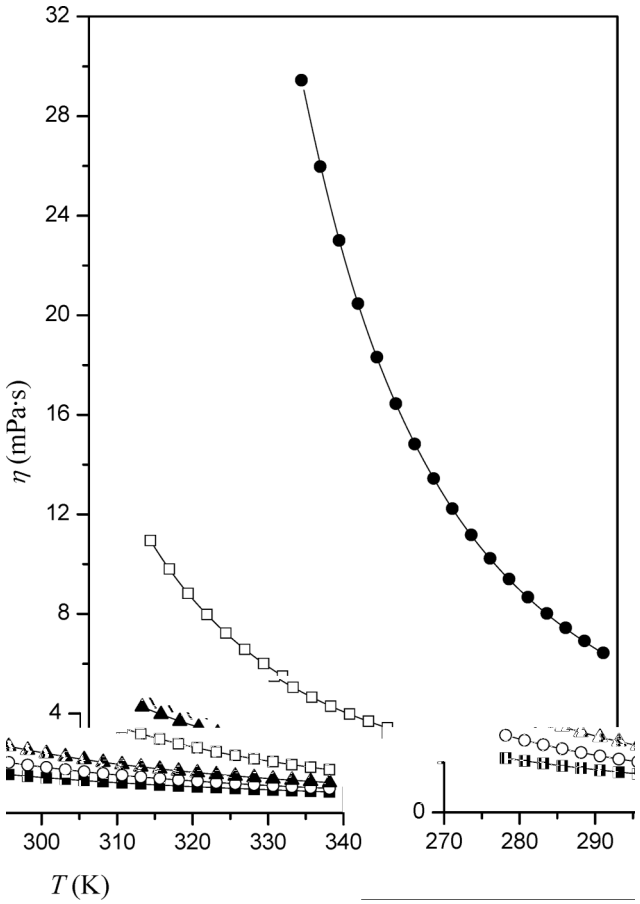


**Fig. 8** Dynamic viscosity as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) Vogel–Fulcher–Tamman's equation.

an important characteristic for applications in extractions of biphasic catalysis. In this case, we have found similar values of log *P* for furfural, furfuryl alcohol and ethyl levulinate. Levulinic acid shows the lowest value of this parameter, which is similar to other organic common acids such as acetic acid.[36]

In the next section a comparison between traditional and common solvents used in synthesis has been carried out. These traditional solvents (chloroform, dichloromethane, benzene and toluene) are not considered environmentally friendly and are classified as VOCs, so replacing them with less polluting solvents should be studied. The solvents derived from biomass studied in this work show quite different properties than the above-mentioned traditional solvents.

Density, in g cm$^{-3}$ at 303.15 K, is similar in traditional solvents and the solvents studied; their values are in a small interval between 0.965458 and 1.149478, but in the case of chloroform it is 1.47060, for dichloromethane 1.30777, for benzene 0.86829, and for toluene 0.85754.[37]

In the case of dielectric constant, traditional solvents at 298.15 K present lower values than the solvents studied, being between 2.27 and 8.93 for benzene and dichloromethane, respectively.[37] However, in the chemicals studied here, their dielectric constant is between 10.34 and 47.80 for butyl levulinate and furfural, respectively.

The viscosity, in mPa s, of green solvents derived from biomass shows very high values when compared to traditional solvents. The values of viscosity at 303.15 K are between 1.3639 and 23.0030 for furfural and levulinic acid, respectively, but in the case of chloroform it is 0.514, for dichloromethane 0.393, for benzene 0.5621, and for toluene 0.5232.[37] One of the most important properties of a lubricant is its viscosity. The basic requirement for a lubricant is that it possesses the viscosity necessary at the process temperature, so that, if there are two surfaces in contact, the film of lubricant prevents direct contact. An excessive rise of temperature can cause a dangerous decrease in viscosity of the lubricant so that the oil film may break, in which case there would be contact between the moving surfaces, with the many consequences this always brings. In our case, the viscosity of the solvents is higher than the traditional solvents, and this could be an advantage in this case because the solvents can be heated to higher temperatures.

Traditional solvents such as chloroform, dichloromethane, benzene and toluene present values of refractive index of 1.44293, 1.42115, 1.49792 and 1.49413, respectively.[37] The values of these traditional solvents are similar in comparison to the green solvents studied because our values are in a small interval between 1.426295 for butyl levulinate, 1.419656 for

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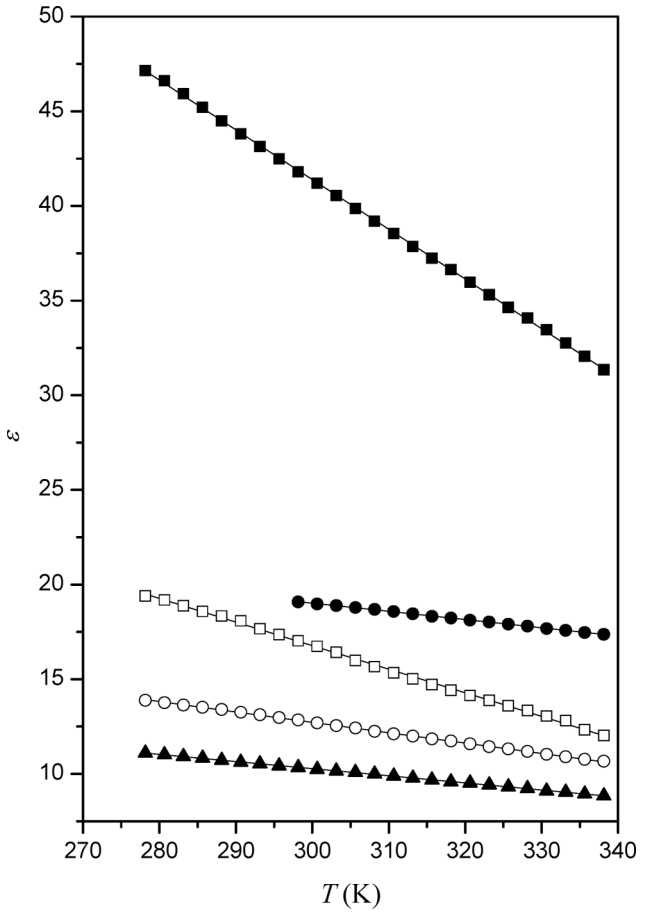


**Fig. 9** Static permittivity as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) eqn (1).

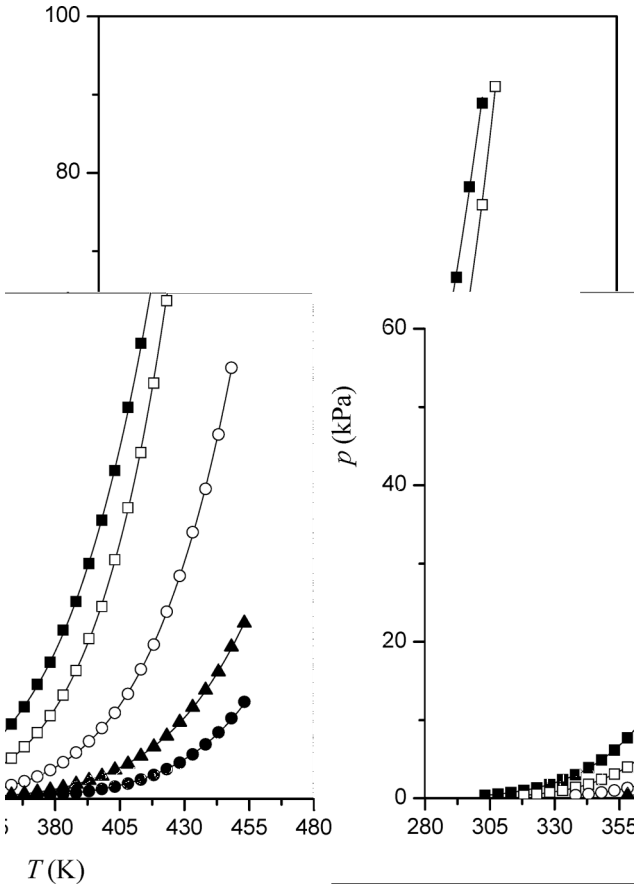


**Fig. 10** Vapour pressure as a function of temperature for the studied green solvents: (■) furfural; (□) furfuryl alcohol; (●) levulinic acid; (○) ethyl levulinate; (▲) butyl levulinate; (—) Antoine's equation.

ethyl levulinate, 1.439701 for levulinic acid, 1.486003 for furfuryl alcohol and 1.523577 for furfural.

The vapour pressure of the green solvents studied is very low. We need to heat the solvents to 383.15 K to obtain this property because some of them could not be measured at room temperature. Their values are 0.615 kPa for levulinic acid, 1.460 kPa for butyl levulinate, 4.690 kPa for ethyl levulinate, 13.280 kPa for furfuryl alcohol and 21.560 kPa for furfural. However, traditional solvents show values of 392.403 kPa in chloroform, 733.011 kPa in dichloromethane, 237.806 kPa in benzene and 91.289 kPa in toluene.[37] These results indicate that the vapour pressures of the green chemicals studied here are much lower than some traditional solvents; therefore, they are thought to have lower VOC character.

## Experimental section

The solvents derived from biomass used in this study were provided by Sigma–Aldrich: furfural, furfuryl alcohol and ethyl levulinate, with a purity of 99%, while the purity of levulinic acid and ethyl levulinate was 98%. The purity of the chemicals was checked by GC chromatography and no further purification was considered necessary. Measurements were performed in a range of temperatures from 278.15 K to 328.15 K with an interval of 2.5 K between each temperature, except in the case of refractive index, whose measurements were carried out from 283.15 K to 328.15 K. It is worth mentioning that the normal melting point of levulinic acid is 310.35 K; therefore, the experimental data obtained for several thermodynamic properties at temperatures lower than the normal melting point correspond to the subcooled liquid.

Densities, $\rho$, and speed of sounds, $u$, of the pure compounds were determined simultaneously with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer, and automatically thermostatted within ±0.001 K. The final uncertainty of density and speed of sound can be estimated at $10^{-6}$ g cm$^{-3}$ and 0.01 m s$^{-1}$, respectively.

Refractive indices at 589.3 nm sodium D wavelength, $n_D$, were measured using a high precision automatic refractometer Abbemat-HP DR. Kernchen whose temperature was internally controlled within ±0.01 K. The uncertainty of the measurements is $1 \times 10^{-6}$.

Surface tensions, $\sigma$, were determined by using a drop volume tensiometer Lauda TVT-2.[18] The temperature was kept constant within ±0.01 K by means of an external Lauda E-200 thermostat. The uncertainty of the surface tension measurement is 0.01 mN m$^{-1}$.

Kinematic viscosities, $\nu$, were determined by using a Schoot–GeräteAVS-440 automatic measuring unit with Ubbelhode viscosimeters of different constants in order to achieve the best accuracy. The uncertainty of the time flow measurements is

±0.01 s, kinetic energy corrections are applied to the experimental data. The temperature was kept constant within ±0.01 K by means of a Schoot–Geräte thermostat. Absolute viscosity, $\eta$, can be obtained from density and kinematic viscosity; the estimated uncertainties range varies from 0.0001 to 0.01 mPa s.

The static permittivities, $\varepsilon$, at a frequency of 2 MHz were obtained using a capacitive measurement method, the capacitances were measured by means of an Agilent 4263BA precision LCR meter connected to a four terminal Agilent 16452A liquid dielectric test fixture through Agilent 16048A test leads. The uncertainty of the permittivity measurements is less than 0.5%. During all measurements, tfi74atmostacted to ±0.01 K by meansofa Schoot–Ge