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Gamma-valerolactone-based solvents

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ABSTRACT

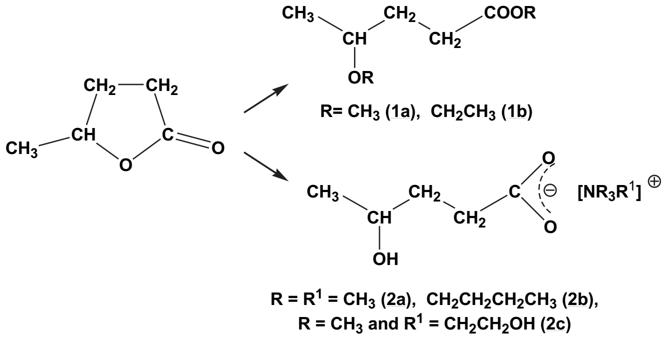
Several γ-valerolactone (GVL) based solvents including methyl 4-methoxyvalerate (**1a**), ethyl 4-ethoxyvalerate (**1b**), tetramethylammonium 4-hydroxyvalerate (**2a**), tetrabutylammonium 4-hydroxyvalerate (**2b**), and cholinium 4-hydroxyvalerate (**2c**) were prepared and characterized.

1. Introduction

The sustainability of the chemical industry and the safe use of chemicals in various applications outside the chemical enterprise require the development of a variety of new solvents, which could be part of a green solvent library to address physical and chemical problems and challenges.[1] Besides the obvious requirements of the physical and chemical properties to perform the solvent functions well, preference should be given to potential molecules that are renewable, biodegradable, and have no or low toxicity according to the fifth principle of green chemistry.[2] Since the total number of readily available and suitable renewable molecules (frequently called bio-molecules, such as bioethanol, bioglycerine, etc.) is rather low, their derivatization could significantly increase the number of available solvents.[3] Accordingly, more and more new derivatives of bioxygenates and even bio-ionic liquids have been prepared and characterized.[4]

We have recently demonstrated that gamma-valerolactone (GVL) can be considered as a sustainable liquid for the production of chemicals and energy.[5] The physical and chemical properties of GVL make it an excellent candidate as a solvent as well. Since GVL is renewable, non-toxic and biodegradable, we have developed two types of derivatives of GVL that can be used as solvents (Scheme 1). The methyl 4-methoxyvalerate (**1a**) and the ethyl 4-ethoxyvalerate (**1b**) can be considered as bio-oxygenates. While the tetramethylammonium 4-hydroxyvalerate (**2a**) and the tetrabutylammonium 4-hydroxyvalerate (**2b**) are partially bio-ionic liquids, the cholinium 4-hydroxyvalerate (**2c**), which was prepared on the basis of the excellent work of Fukaya et al.,[4] is a true bio-ionic liquid.

The synthesis, structural characterization, and some of the physical properties of the GVL-based solvents are reported.



Scheme 1.

2. Synthesis and characterization

2.1. Synthesis and characterization of alkyl-4-alkyloxyvalerates

Although there are several synthetic protocols available for the synthesis of alkyl-ether-esters,[6] we have used the acid catalyzed addition of trialkyl orthoformates ($CH(OR)_3$: R=Me or Et) to GVL in the corresponding alkyl alcohols (ROH: R=Me or Et) for the synthesis of methyl 4-methoxyvalerate (**1a**) and ethyl 4-ethoxyvalerate (**1a**).[6c] The aqueous biphasic purification resulted in 89 and 90% yields for **1a** and **1b**, respectively. Their structure was confirmed by GC–MS, and ^1H and ^{13}C NMR spectroscopy (see Supplementary data). We have also established the temperature dependence of the vapor pressure of **1a** and **1b** (Table 1), a key solvent property to control VOC emission in general.[7]

The vapor pressure of **1b** is lower than that of **1a** at all temperatures as expected. In comparison to other oxygenates, it appears that both **1a** and **1b** have higher vapor pressure than that of GVL,[4] but significantly lower than the other oxygenates including methanol,[8] ethanol,[8] MTBE,[9] and ETBE[9] (Fig. 1).

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Table 1
Vapor pressure of **1a** and **1b**

Temperature (°C)	**1a** (kPa)	**1b** (kPa)
0	2.57	1.92
25	3.91	—
50	5.45	4.10
75	8.80	—
100	13.75	10.50
125	22.32	—
150	31.7	21.75

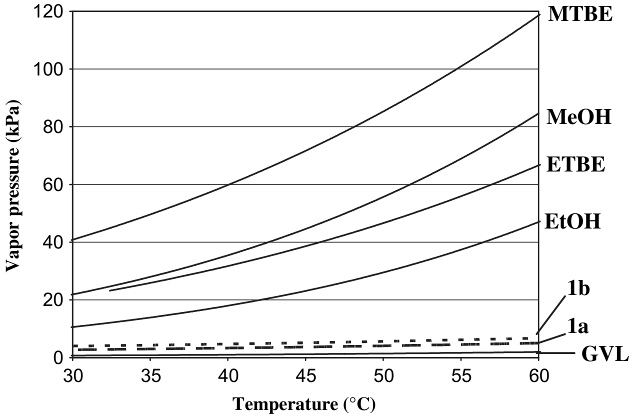
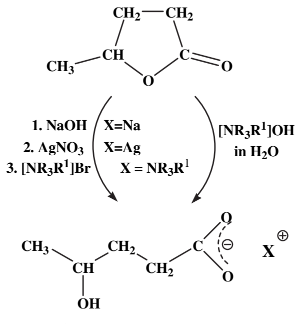


Figure 1. Vapor pressure of oxygenates.

It should be also noted, that in the presence of 1% and 10% water, **1a** and **1b** did not hydrolyze at neutral pH after 24 h at 100 °C. However, in the presence of acids or bases the hydrolysis is slow but detectable (few % conversion after several hours) and the formation of GVL and the corresponding alcohol was observed. While this could limit some of the applications, the use of **1b** seems especially environmentally friendly as its decomposition would result in EtOH and GVL.

2.2. Synthesis and characterization of tetraalkylammonium and colinium 4-hydroxyvalerates

Originally we have tried to prepare the GVL-based ionic liquid tetraalkylammonium 4-hydroxyvalerates by the replacement of the sodium to silver cation in the sodium 4-hydroxyvalerate followed by the reaction with tetraalkylammonium bromide resulting in silver bromide precipitate and the wet ionic liquid. While the synthesis indeed resulted in ionic liquids, the protocols were rather challenging as the presence of the silver required that all manipulations had to be performed in the dark. In addition the filtration of the silver salt was very difficult (especially as their presence even in small amounts resulted in black coloration under lights).



R = R^1 = CH$_3$ (2a), CH$_2$CH$_2$CH$_2$CH$_3$ (2b),
R = CH$_3$ and R^1 = CH$_2$CH$_2$OH (2c)

The alternative procedure was based on the reaction of the aqueous solution of tetraalkylammonium hydroxides with GVL at room temperature resulting in an aqueous solution of the required products, which were isolated in good yields (>99%) by removing the water under reduced pressure at 80 °C. The structure of **2a**–**c** was confirmed by ^{1}H and ^{13}C NMR (see Supplementary data) and the temperature dependence of several physical properties were measured.

The densities of **2a**–**c** decreased linearly (with a correlation factor higher than 0.98) when the temperature was increased, as expected (Fig. 2). The density values show that the presence of a larger tetraalkylammonium cation results in lower density.[10]

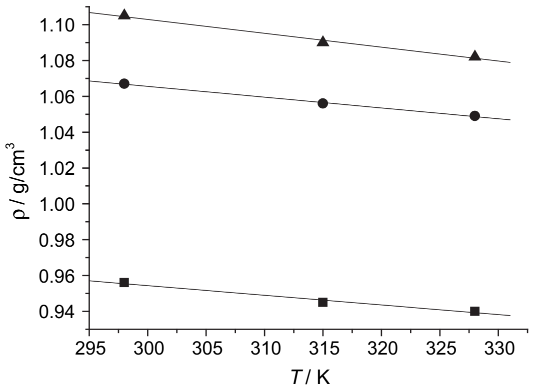


Figure 2. Density of **2a** (●), **2b** (■), **2c** (▲).

The viscosity of **2a**–**c** decreased exponentially (with a correlation factor higher than 0.99) when the temperature was increased (Fig. 3). The measured viscosities at 25 °C (**2a**: 90.49±0.09 cP; **2b**: 65.12±0.14 cP; **2c**: 75.52±0.14 cP) were at the expected values for similar ionic liquids.[11] The activation energies for viscous flow of **2a**–**c** were 50.78 kJ, 53.53 kJ, and 46.28 kJ, respectively. These values are higher than normal liquids and liquid salts with higher melting points.[12]

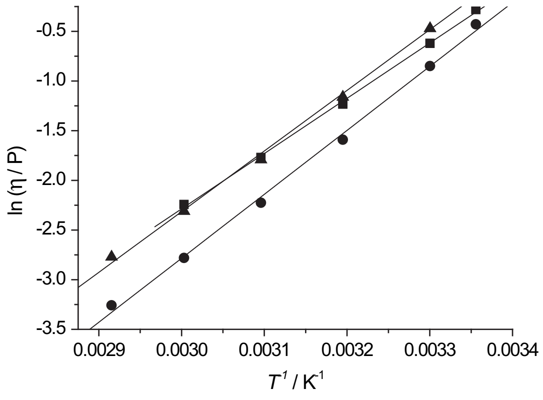


Figure 3. Viscosity of **2a** (▲), **2b** (●), **2c** (■).

The conductivity of **2a**–**c** increased exponentially (with a correlation factor higher than 0.99) when the temperature was increased (Fig. 4). The measured conductivities at 25 °C (**2a**: 0.643 mS/cm; **2b**: 0.199 mS/cm; **2c**: 0.385 mS/cm;) were similar to quaterner ammonium salts.[10] The activation energies of conductivity of **2a**–**c** were 41.06 kJ, 44.30 kJ, and 42.74 kJ, respectively. These values are higher than normal liquids and liquid salts with higher melting points.[13]

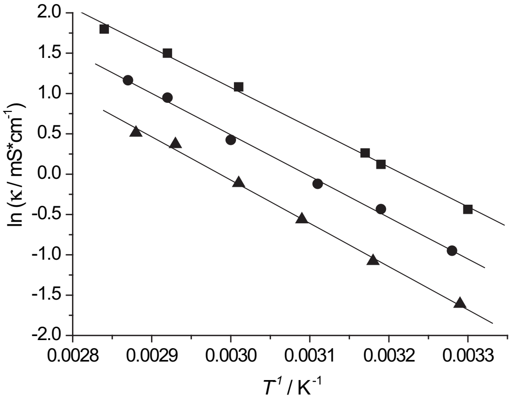


Figure 4. Conductivity of **2a** (■), **2b** (▲), **2c** (●).

The vapor pressures of these ionic liquids were rather low at 0 °C, but rapidly increased with increasing temperature (Fig. 5).

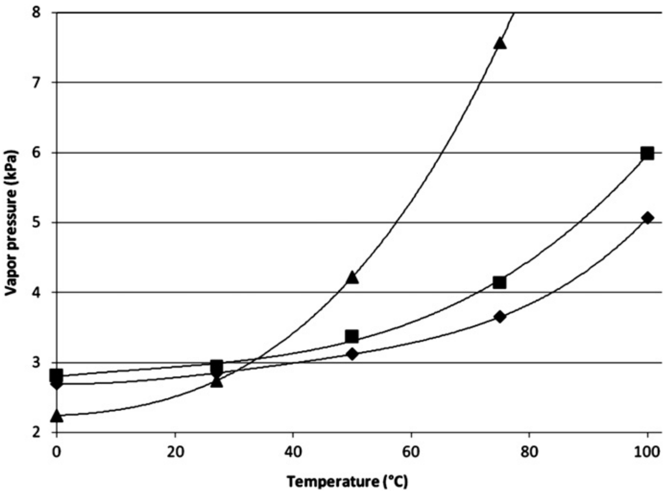


Figure 5. Vapor pressure of **2a** (■), **2b** (◆), **2c** (▲).

A very rapid decomposition took place at 125 °C for **2a** and **2b**, and at 100 °C for **2c**. GC–MS analysis of the head-space after the decomposition revealed the presence of NMe_3 and NBu_3 for **2a** and **2b**, $Me_2NCH_2CH_2OH$ for **2c**, GVL, and CO_2, besides some unidentified compounds.

In conclusion, we have prepared two types of derivatives of GVL that can be used as solvents (Scheme 1). The methyl 4-methoxyvalerate (**1a**) and the ethyl 4-ethoxyvalerate (**1b**) can be considered as bio-oxygenates. While the tetramethylammonium 4-hydroxyvalerate (**2a**) and the tetrabutylammonium 4-hydroxyvalerate (**2b**) are partially bio-ionic liquids, the cholinium 4-hydroxyvalerate (**2c**) is a bio-ionic liquid. Evaluation of these solvents in synthesis and other applications is in progress.

3. Experimental

3.1. General

All chemicals were used as received. NMR measurements were recorded on a Bruker Avance 250 spectrometer. The density was measured by the pycnometer method. A Höppler viscosimeter was used to obtain the viscosity data. Conductivity data were measured with a Radelkis OK-114 conductometer, calibrated with 0.01 mol KBr solution, using standard procedures.

3.2. Methyl 4-methoxyvalerate (1a)

A solution of 3 g (30 mmol) γ-valerolactone, 6.36 g (60 mmol) trimethylorthoformate, 0.1 ml sulfuric acid in 30 mL methanol was stirred for 24 h at 50 °C. Methanol was removed in vacuo, and a 30 mL saturated solution of $NaHCO_3$ and 30 mL EtOAc was added to the solid or liquid residue. After phase separation, the organic layer was dried over Na_2SO_4, the solvents were removed under reduced pressure, and the crude product was purified by vacuum transfer in a Kugelrohr apparatus. The product was a colorless liquid (refractive index: 1.3960 at 20 °C). Yield: 3.89 g (89%). ^{1}H NMR ($CDCl_3$) δ: 1.09 (d, *J*=6.0 Hz, 3H), 1.75 (m, 2H), 2.34 (t, *J*=7.5 Hz, 2H), 3.29 (m, 1H), 3.25 (s, 3H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 19.2, 30.3, 31.7, 51.8, 56.4, 76.1, 174.5.

3.3. Ethyl 4-ethoxyvalerate (1b)

Same procedure as above using 2 g (20 mmol) GVL, 5.92 g (40 mmol) triethylorthoformate, 0.1 mL sulfuric acid in 30 mL EtOH, 30 mL saturated solution of $NaHCO_3$, and 30 mL EtOAc. The product was a colorless liquid (refractive index: 1.3942 at 20 °C). Yield: 3.20 g (92%). ^{1}H NMR ($CDCl_3$) δ: 1.11 (d, *J*=6.2 Hz, 3H), 1.13 (t, *J*=7.1 Hz, 3H), 1.22 (t, *J*=7.1 Hz, 3H), 1.73 (m, 2H), 2.35 (m, 2H), 3.35 (m, 2H), 3.50 (m, 1H), 4.08 (q, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.6, 15.9, 20.0, 30.8, 32.0, 60.6, 64.1, 74.4, 174.2.

3.4. Tetramethylammonium-4-hydroxyvalerate

A solution of 9.12 g tetramethylammonium hydroxide (0.1 mol) in 27.35 g water (25% solution) and 10.015 g γ-valerolactone (0.1 mol) was stirred for 1 h. The water was removed under reduced pressure at 80 °C. The remaining product was a yellow liquid (refractive index: 1.4483 at 20 °C). Yield: 19.04 g (99.5%). ^{1}H (250.13 MHz, DMSO-d_6) δ: 0.95 (d, *J*=6.16 Hz, 3H), 1.44 (q, *J*=6.63 Hz, 2H), 1.99 (m, 2H), 3.13 (s, 12H), 3.53 (sx, *J*=5.83 Hz, 1H), ^{13}C (DMSO-d_6) δ: 24.0; 35.5; 36.2; 54.3 (t, *J*=3.9 Hz); 67.0; 177.3.

3.5. Tetrabutylammonium-4-hydroxyvalerate

A solution of 25.99 g tetrabutylammonium hydroxide (0.1 mol) in 59.00 g water and 10.012 g γ-valerolactone (0.1 mol) was stirred for 1 h. The water was removed under reduced pressure at 80 °C. The product was a light yellow liquid (refractive index: 1.4485 at 20 °C). Yield: 35.950 g (99.9%). ^{1}H NMR (acetone-d_6) δ: 0.98; (d, *J*=6.63 Hz, 3H), 1.00(t, 12H), 1.40 (sx, *J*=7.27 Hz, 8H) 1.51 (q, *J*=6.00 Hz, 2H), 1.78 (qn, *J*=7.37 Hz, 8H), 2.23 (m, 2H), 3.45 (t, *J*=8.38 Hz, 8H), 3.56 (sx, *J*=5.21 Hz, 1H). ^{13}C NMR (acetone-d_6) δ: 14.9; 21.3; 25.4, 25.9; 37.1; 38.7; 60.1 (t, *J*=2.76 Hz); 70.0; 179.6.

3.6. Cholinium 4-hydroxyvalerate

A solution of 12.1 g cholinium hydroxide (0.1 mol) in 12.1 g water (50% solution) was stirred with 10.02 g γ-valerolactone (0.1 mol) at 25 °C for 1 h. Removal of the water at 80 °C under reduced pressure resulted in a red liquid as the final product (refractive index: 1.4570 at 20 °C). Yield: 21.962 g (99.2%). ^{1}H NMR (DMSO-d_6) δ: 0.97 (d, *J*=6.63 Hz, 3H), 1.46 (q, *J*=6.00 Hz, 2H), 2.00 (m, 2H), 3.12 (s, 9H), 3.42 (t, *J*=5.21 Hz, 2H), 3.55 (sx, *J*=6.32 Hz, 1H), 3.82 (qn, *J*=4.11 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 24.0; 35.4; 35.9; 53.1(t, *J*=3.7 Hz); 55.0; 67.0; 67.2 (t, *J*=2.8 Hz); 177.3.

3.7. Vapor pressure measurement

The vapor pressure was measured with a Rosemount manometer attached to a 4 mL Hasteloy-C reactor system. After placing 2 mL of the sample in the reactor with a magnetic stirrer, the manometer was connected, the reactor was placed in a 0 °C ice-water mixture and the sample was stirred. The reactor was evacuated, and the pressure value was recorded after the reactor reached the thermal equilibrium. Higher temperatures were achieved by using a heated oil bath and data were recorded after reaching thermal equilibrium.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.11.013.

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