Electronics Supplementary Information

Deep eutectic solvents choline chloride·2CrCl₃·6H₂O: an efficient catalyst for esterification of formic and acetic acid at room temperature

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1. Experimental section

**Materials.** All reagents and solvents for syntheses were purchased from commercial sources and used without further purification.

**Measurements.** The analysis of the reaction mixture was carried out on a gas chromatograph (sp-6890) equipped with a flame ionization detector (FID) and a capillary column (HP-5, 30 m×0.25 mm×0.25 mm). The column temperature was 80 °C. The temperatures of the injector and detector were maintained at 320 °C and 320 °C, respectively. The products were further identified by GC (varian 3900)–MS (varian saturn 2100 T) quipped with a flame ionization detector (FID) and a capillary column (DB-5, 30 m×0.25 mm×0.25 mm). The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400MHz NMR spectrometer at 298K. The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (TMS, 0 ppm for $^1$H), CDCl$_3$ (77.3 ppm for $^{13}$C).
Preparation of deep eutectic solvent \([\text{ChCl}][\text{CrCl}_3\cdot6\text{H}_2\text{O}]_2\). A mixture of the chromium(iii) chloride hexahydrate (CrCl\(_3\cdot6\text{H}_2\text{O}\)) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a green liquid formed.

Preparation of deep eutectic solvent \([\text{ChCl}][\text{FeCl}_3]_2\). A mixture of the ferric chloride (FeCl\(_3\)) and choline chloride in a molar ratio of 2:1 was heated to 100°C with gentle stirring until a dark brown liquid formed.

Preparation of deep eutectic solvent \([\text{ChCl}][\text{AlCl}_3\cdot6\text{H}_2\text{O}]_2\). A mixture of the aluminum chloride hexahydrate (AlCl\(_3\cdot6\text{H}_2\text{O}\)) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a colorless liquid formed.

Preparation of deep eutectic solvent \([\text{ChCl}][\text{MgCl}_2\cdot6\text{H}_2\text{O}]_2\). A mixture of the magnesium chloride hexahydrate (MgCl\(_2\cdot6\text{H}_2\text{O}\)) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a green clear liquid formed.

Preparation of deep eutectic solvent \([\text{ChCl}][\text{MnCl}_2\cdot4\text{H}_2\text{O}]_2\). A mixture of the manganese(II) chloride tetrahydrate (MnCl\(_2\cdot4\text{H}_2\text{O}\)) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a pink liquid formed.

Preparation of deep eutectic solvent \([\text{ChCl}][\text{CoCl}_2\cdot6\text{H}_2\text{O}]_2\). A mixture of the cobalt(II) chloride hexahydrate (CoCl\(_2\cdot6\text{H}_2\text{O}\)) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a blue liquid formed.
Preparation of deep eutectic solvent $[\text{ChCl}]\left[\text{NiCl}_2\cdot6\text{H}_2\text{O}\right]_2$. A mixture of the nickel chloride hexahydrate ($\text{NiCl}_2\cdot6\text{H}_2\text{O}$) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a green liquid formed.

Preparation of deep eutectic solvent $[\text{ChCl}]\left[\text{CuCl}_2\cdot2\text{H}_2\text{O}\right]_2$. A mixture of the cupric chloride ($\text{CuCl}_2\cdot2\text{H}_2\text{O}$) and choline chloride in a molar ratio of 2:1 was heated to 70°C with gentle stirring until a brown liquid formed.

Preparation of deep eutectic solvent $[\text{ChCl}]\left[\text{ZnCl}_2\right]_2$. A mixture of the Zinc chloride ($\text{ZnCl}_2$) and choline chloride in a molar ratio of 2:1 was heated to 100°C with gentle stirring until a colorless liquid formed.

Preparation of deep eutectic solvent $[\text{ChCl}]\left[\text{SnCl}_2\right]_2$. A mixture of the anhydrous stannous chloride ($\text{SnCl}_2$) and choline chloride in a molar ratio of 2:1 was heated to 100°C with gentle stirring until a colorless liquid formed.

The synthesis process of $n$-butyl acetate. Carboxylic acids (0.10 mol 6.00g) and $n$-butanol (0.02 mol 1.48g) without solvent were added, and then the deep eutectic solvent $[\text{ChCl}]\left[\text{CrCl}_3\cdot6\text{H}_2\text{O}\right]_2$ (0.5mmol 0.3365g) was added to initiate the reaction. The reaction mixture was stirred at 25°C for 24h. After the reaction was completed, two clearly separated phases are formed, the upper liquid layer was spilled off with a Pasteur pipette, the lower layer formed by DES, water and excess starting material was extracted with diethyl ether three times. The combined organic layers were washed with saturated aqueous $\text{NaHCO}_3$ three times and dried over anhydrous $\text{Mg}_2\text{SO}_4$, filtered, and then the solvent was removed by rotary evaporation to obtain $n$-butyl acetate 1.99g (isolated yield=85.7%).
Recycle process of DES. After the reaction was completed, two clearly separated phases are formed, the upper liquid layer was spilled off with a Pasteur pipette, the lower layer formed by DES, water and excess starting material was extracted with diethyl ether three times. A drying in vacuo at 60°C overnight was carried out on DES for further cycles.

2. The calculation of the yield n-butyl acetate by GC

The yield of esters and the selectivity to esters was calculated using equations (1-2), via GC with 1,4-dimethyl-benzene as internal standard, in which the number of moles was determined by Internal Standard Method from the chromatographic analysis (BA-n-butyl acetate, PX-1,4-dimethyl-benzene) (n-butyl acetate’s standard curve: y=1.9754x-0.0500 with R²=0.9997, where y=m_{BA}/m_{PX} and x=A_{BA}/A_{PX} with A being the integral area of GC).

\[ m_{BA} = m_{PX} \times (1.9754 \times \frac{A_{BA}}{A_{PX}} - 0.0500) \]  

(1)

\[ \text{Yield}_{BA} = \frac{m_{BA}}{116} \times 74 \times 100\% \]  

(2)

After the reaction was completed, liquid samples were analyzed on a gas chromatograph after addition of the internal standard. The yield of n-butyl acetate was calculated using equations (1-2).

3. Representative examples of GC chromatograms from reaction mixtures
Fig S1 Representative examples of GC chromatograms from reaction mixtures

4. Characterization data and spectra for n-butyl acetate

$\delta_\text{H} (400 \text{ MHz, CDCl}_3)$ 4.01, 1.99, 1.56, 1.34, 0.89. $\delta_\text{C} (101 \text{ MHz, CDCl}_3)$ 171.33, 64.37, 30.57, 20.87, 19.05, 13.60.
5. The effect of temperature on the esterification reaction with \([\text{ChCl}] \ [\text{FeCl}_3]_2\)
Table S1 The effect of temperature on the esterification reaction with [ChCl] [FeCl$_3$]$_2$\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature</th>
<th>Yield of n-butyl acetate \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25°C</td>
<td>64.5%</td>
</tr>
<tr>
<td>2</td>
<td>30°C</td>
<td>66.9%</td>
</tr>
<tr>
<td>3</td>
<td>40°C</td>
<td>71.3%</td>
</tr>
<tr>
<td>4</td>
<td>50°C</td>
<td>78.4%</td>
</tr>
<tr>
<td>5</td>
<td>60°C</td>
<td>79.9%</td>
</tr>
<tr>
<td>6</td>
<td>70°C</td>
<td>79.5%</td>
</tr>
<tr>
<td>7</td>
<td>80°C</td>
<td>78.5%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: n-butanol (0.01 mol), acetic acid (0.05 mol), and DES (0.25 mmol) for 24h
\textsuperscript{b} Yield are based on GC. 1,4-dimethyl-benzene as internal standard

6. The GC-MS spectra of esters  (Table 4)

(1) The GC-MS spectra of ethyl acetate
The GC-MS spectra of n-propyl acetate
The GC-MS spectra of isopropyl acetate
The GC-MS spectra of n-butyl acetate
(5) The GC-MS spectra of isoamyl acetate
(6) The GC-MS spectra of n-hexyl acetate
(7) The GC-MS spectra of n-octyl acetate
(8) The GC-MS spectra of iso-octyl acetate
iso-octyl alcohol

acetic acid

iso-octyl acetate
(9) The GC-MS spectra of cyclohexyl acetate
The GC-MS spectra of phenyl acetate
The GC-MS spectra of butyl formate

(11) The GC-MS spectra of butyl formate
The GC-MS spectra of butyl propionate
butyl propionate

butonal

Propanoic acid
The GC-MS spectra of butyl butyrate

Butonal

Butyric acid

Butyl
The GC-MS spectra of 2-chloroethyl acetate
The GC-MS spectra of propargyl acetate
Propargyl alcohol

Propargyl acetate

Acetic acid
The GC-MS spectra of isoamyl formate

- Isoamyl formate
- Formic acid
- Isoamyl alcohol
(17) The GC-MS spectra of n-hexyl formate

![GC-MS spectrum of n-hexyl formate, formic acid, n-hexanol](image)
The GC-MS spectra of n-octyl formate
n-hexyl formate
Formic acid
n-Octanol
The GC-MS spectra of benzyl formate

- Benzyl formate
- Formic acid
- Benzyl alcohol