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Dihydrolevoglucosenone (Cyrene™), a Bio-based Solvent for Liquid-Liquid Extraction Applications

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Abstract

Dihydrolevoglycosenone, commercially known as Cyrene™, is a versatile bio-based solvent reported for various applications including being a medium of chemical reactions and membrane manufacture. In this work, application of Cyrene™ in liquid-liquid extractions has been investigated. Four ternary systems have been assessed at 298.15K, 323.15K and 348.15K, keeping Cyrene™ and methylcyclohexane constant and changing the third compound to toluene, cyclohexanol, cyclohexanone and cyclopentyl methyl ether. Studying these selected ternary systems, yielded an indication of applicability of Cyrene™ in related industrial separation processes such as aromatic/aliphatic separations, and in separations of oxygenates in the cyclohexane oxidation process. Key factors are biphasic system formation, distribution coefficients and selectivity. All ternary systems showed type I liquid-liquid phase behavior with a selective extraction of ternary components from methylcyclohexane by Cyrene™. The highest selectivity at 298.15K was found for cyclohexanol with 61.4±4.33, followed by cyclohexanone with 44.1±8.63, while toluene and cyclopentyl methyl ether had a selectivity of respectively 12.0±0.89 and 6.4±0.08. Although Cyrene™ is applicable in all four ternary systems, the miscibility gap is narrow for the oxygenated species,
indicating a limited operation window for liquid-liquid extraction which will be more severe at higher temperatures. Overall, the studies showed that there are certainly application windows for Cyrene™. In the case of oxygenate extraction, a process with Cyrene™ appears energy-saving because the energy duty appears to be lower than when using water, the best alternative solvent, which is a low boiling solvent for this purpose.

KEYWORDS: Dihydrolevoglucosenone, Cyrene™, Bio-based Solvent, Liquid-Liquid Equilibrium, Liquid-Liquid Extraction

Introduction

Insights in the liquid-liquid extraction (LLX) applicability of dihydrolevoglycosenone, or Cyrene™, was obtained by performing LLX in four different ternary systems. Cyrene™, a bio-based polar solvent, attracted recent attention as being versatile for various applications, e.g. as a medium to perform chemical reactions\(^1\)\(^-\)\(^7\) and to prepare membranes by phase inversion\(^8\), though no mention for LLX applications has been found as of yet.
Cyrene™ can be an alternative aprotic dipolar solvent\textsuperscript{1-8}, solvents of this class are typically used in a range of molecular separations, from aromatic/aliphatic separation\textsuperscript{9-11} to carboxylic acid separation from water.\textsuperscript{12} Industrially important members of the solvent class of aprotic dipolar solvents include N-methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF), which both are considered toxic solvents and subject to restrictive legislation. \textsuperscript{13-15} Cyrene™ is reported to have a much lower toxicity\textsuperscript{16-17}, and additionally since it is a biobased product, it offers chances for the chemical industry to reduce the consumption of fossil oil by replacing their toxic fossil oil-based solvents for a much more benign biobased alternative.\textsuperscript{18} In a recent communication, the Circa Group announced a production capacity of Cyrene™ of 1 kton per annum, which signifies the mass production of this new biobased solvent.\textsuperscript{19} Although, bulk prices may not be publically available, Krishna et al. state that the bulk price of Cyrene™ may be approximately to be 2 €/kg \textsuperscript{20} which is comparable with traditional solvents.

Two key classes of molecular separation processes using solvents include extractive distillation (ED) and LLX. In another article\textsuperscript{21}, we showed the potential of Cyrene™ as entrainer in ED of aromatic/aliphatic mixtures and paraffin/olefin mixtures. Similarly, next to the already proven entrainer function in extractive distillations, Cyrene™ may
be useful for LLX as well. In order to investigate the applicability of Cyrene™ in LLX processes, we assessed the liquid-liquid equilibrium (LLE) behavior of several ternary systems formed with Cyrene™. The investigated systems include (1) methylcyclohexane (MCH) and toluene (TOL), (2) MCH and cyclohexanol (CHOH), (3) MCH and cyclohexanone (CHO) and (4) MCH and cyclopentyl methyl ether (CPME).

The molecular structures of all species used in this study are displayed in figure 1.

![Molecular structures of species](image)

**Figure 1.** Structures of the molecules used in this study.

These ternary mixtures have specifically been chosen to firstly represent aromatics/aliphatics separations. These separations using LLX has been subject of study for a variety of model compounds, including benzene, toluene, xylenes, (methyl)cyclohexane and n-alkanes. The model systems vary as the related industrial mixture is complex. The results in this study on liquid-liquid equilibria with
Cyrene™, MCH and TOL will be compared to the elaborate work done in the past concerning molecular solvents\textsuperscript{22-24}, ionic liquids (ILs)\textsuperscript{25,29-30} and deep eutectic solvents (DESs).\textsuperscript{31-33}

The separation of alcohols and ketones from aliphatics was chosen because the compounds possess either an alcohol or a ketone functionality, and they are relevant industrial chemicals, for example in the industrial oxidation process of cyclohexane to CHO and CHOH\textsuperscript{34-35}. Kim et al. and Pei et al. investigated similar systems with CHO and CHOH, though used cyclohexane as hydrocarbon and studied dimethyl sulfoxide (DMSO) and water as a solvent\textsuperscript{36-37}.

The last ternary mixture with MCH and CPME was chosen for the CPME ether functionality. CPME also has the potential of being a biobased solvent\textsuperscript{38-40}. The extraction of CPME from an aliphatic stream has not been studied yet.

Next to evaluation of the extraction performance of Cyrene™ for each of the systems, the LLE were also correlated using the UNIQUAC model. Lastly, by maintaining MCH as the constant, it became possible to compare all the systems with each other and investigate trends between different functional groups, and thus study the applicability of Cyrene™ for separating molecules with these different functional groups.
Experimental Section

Materials

Chemicals, if not otherwise specified, were used as received without any additional purification. Cyclopentyl methyl ether (≥ 99.9%), cyclohexanone (≥ 99.9%) and cyclohexanol (99%) were obtained from Sigma Aldrich, while methylcyclohexane (Reagent Grade, 99%) was purchased from Honeywell. Toluene (ACS, reag.Ph.Eu) was procured from VWR Chemicals, while analytical acetone (LiChrosolv®) was acquired from Merck. A 1L bottle of dihydrolevoglucosenone, or Cyrene™, (99.3%) was supplied by the Circa Group.

Liquid-Liquid Extraction Procedure

For the liquid-liquid extraction experiments closed 10mL glass vials were used. All compounds were weighed with an accuracy of 0.5 mg on an analytical balance. Consecutively a vortex mixer and a temperature-controlled shaking bath were used in the equilibration. The mixture was shaken at 200 rpm for at least 12h at a constant temperature and subsequently settled for at least 1h prior to sample-taking. The experiments were conducted at 298.15K, 323.15K or 348.15K with a temperature variation of 0.02K. A solvent to feed ratio on mass basis of 1 was maintained and the
total mass of each phase was kept approximately at 3 grams. A sample of 0.5-1.0 mL
was taken with a 2mL syringe with an injection needle from both phases. Both phases
were analyzed following the analysis produce.

**Analysis Procedure**

A Thermo Scientific Trace 1300 gas chromatograph with two parallel ovens and
an autosampler TriPlus for 100 liquid samples was used for the analyses. Each system
was analyzed using an Agilent DB-1MS column (60m × 0.25mm × 0.25μm) with an
injection volume of 1 μl diluted in analytical acetone. The same instrumental method
was used for every system with a ramped temperature profile following the program of
initial temperature at 50°C, followed by a direct ramp of 10 °C/min to 200°C. The
second ramp, which was directly initiated after reaching 200°C, of 50 °C/min to 320 °C
finished the program, which lasts 20 min. The FID temperature was 330°C. A column
flow of 2 ml/min with a split ratio of 5, an airflow of 350 ml/min, a helium make-up flow
of 40 ml/min and a hydrogen flow of 35 ml/min were used.

**Fitting Procedure**
Each ternary system was correlated for all temperatures simultaneously with the
UNIQUAC model. This model predicts the activity coefficient as the summation of the
combinatorial ($γ_i^c$) and residual ($γ_i^R$) term of the activity coefficient, see equation 1.41

$$\ln γ_i = \ln γ_i^c + \ln γ_i^R$$

(1)

The combinatorial term, using the Guggenheim-Stavermann approximation42,
accounts for the influence of shape differences between the molecules and the
corresponding entropy effects. This contribution of the activity coefficient is elaborated
in equations 2, 3 and 4.

$$\ln γ_i^c = \ln \left(\frac{Φ_i}{x_i}\right) + 1 - \frac{Φ_i}{x_i} - 5q_i\left(\ln \left(\frac{Φ_i}{θ_i}\right) + 1 - \frac{Φ_i}{θ_i}\right)$$

(2)

$$Φ_i = \frac{x_i r_i}{\sum_j x_j r_j}$$

(3)

$$θ_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

(4)

Where, $Φ_i$ is the volume fraction, $θ_i$ is the surface area fraction, $x_i$ is the molar fraction
and the Van der Waals volume, $r_i$, and surface area, $q_i$, of each component.

The residual term, see equations 5 and 6, is determined using the same parameters,
and the additional empirical binary interaction parameters $τ_{ij}$. This value is fitted using
the temperature independent parameter \((A_{ij})\) and temperature-dependent parameter \((B_{ij})\).

\[
\ln \gamma_i^R = q_i \left(1 - \ln \left(\frac{\sum_j q_j x_{ij}}{\sum_j q_j x_j}\right) - \frac{\sum_j q_j x_{ij}}{\sum_k q_k x_k \tau_{kj}}\right) \tag{5}
\]

\[
\tau_{ij} = A_{ij} + \frac{B_{ij}}{T(K)} \tag{6}
\]

For the correlation, known Van der Waals volumes and surface areas were used, see table 1. For Cyrene\textsuperscript{TM}, the parameters were not available in the literature, and were estimated with Density Functional Theory with a B3LYP 6-311+G** parameterization in combination with the methodology of Banerjee et al.\textsuperscript{43}

**Table 1.** Van der Waals volumes and surface areas of all components

<table>
<thead>
<tr>
<th>Component</th>
<th>(r_i)</th>
<th>(q_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylcyclohexane\textsuperscript{22}</td>
<td>5.174</td>
<td>4.396</td>
</tr>
<tr>
<td>Toluene\textsuperscript{44}</td>
<td>3.920</td>
<td>2.970</td>
</tr>
<tr>
<td>Cyclohexanol\textsuperscript{97}</td>
<td>4.274</td>
<td>3.284</td>
</tr>
<tr>
<td>Cyclohexanone\textsuperscript{97}</td>
<td>4.114</td>
<td>3.340</td>
</tr>
<tr>
<td>CPME\textsuperscript{45}</td>
<td>4.214</td>
<td>3.248</td>
</tr>
<tr>
<td>Cyrene\textsuperscript{TM}</td>
<td>4.843</td>
<td>3.322</td>
</tr>
</tbody>
</table>

**Results and Discussion**
The four ternary LLE systems that were investigated in this study are presented in a subsection for each of the systems. All of the systems showed type I phase behavior for all temperatures investigated. For each of the ternary systems the selectivity \( S_{ij} \) of the solute (i), being toluene, cyclohexanol, cyclohexanone or CPME, over MCH (j) was examined (equation 8). This selectivity is defined as the ratio of the distribution coefficients \( K_{D,i} \) of each of the solutes, which in turn is defined as the ratio of the concentration of the solute, on a weight basis, in the solvent \( ([X_i]_s) \) and the organic phase \( ([X_i]_o) \) as in equation 7.

\[
K_{D,i} = \frac{[X_i]_S}{[X_i]_O} \tag{7}
\]

\[
S_{ij} = \frac{K_{D,i}}{K_{D,j}} \tag{8}
\]

All experimental results have been correlated using the UNIQUAC model, which was checked on its thermodynamic consistency using the Hessian Matrix test. This information is provided in the Supporting Information (SI), as well as tables with all the measured data and calculated distribution coefficients and selectivities. This allows an approximate description of the binodal curve and the tielines. After describing the results for each of the ternary systems individually, in the last subsection, all ternary systems are compared to enable a general description of the affinities of Cyrene\textsuperscript{TM}.
towards different moieties. Additionally, rough short-cut calculations were performed
of the combined CHOH/MCH and CHO/MCH cases to assess the potential of Cyrene™
in a LLX process. In the SI, all the weight fractions, distribution coefficients and
selectivities of the ternary diagrams are displayed and/or tabled.

**Methylcyclohexane – Toluene - Cyrene™**

The results for the MCH – toluene – Cyrene™ ternary system are displayed in figure
2. As can be seen from the binodal curves, a significant miscibility region can be seen.

For 298.15K, only below ~35 wt. % toluene a biphasic system is observed, which
further reduces with increasing temperatures. This is in line with our work on extractive
distillation at a temperature above 373K, where no phase splitting was observed for
this system.²¹
Figure 2. The ternary diagrams of the LLE of toluene, MCH and Cyrene\textsuperscript{TM} with the lie-lines, feed compositions and binodal curves at (a) 298.15K, (b) 323.15K and (c) 348.15K, and (d) the S\textsubscript{TOL,MCH} of Cyrene\textsuperscript{TM} at the same temperatures. The UNIQUAC fit is added throughout.

A selectivity of 11.99±0.89 was induced with a toluene concentration of ~0.74 wt. % in the Cyrene\textsuperscript{TM} phase at 298.15K. This selectivity decreases to 6.76±0.65 and
4.91±0.58 at respectively 353.15K and 348.15K for similar toluene concentrations. This is due to a lower activity coefficient of MCH in Cyrene™, a consequence of a polarity decrease of the solvent phase, which is a consequence of the higher hydrocarbon (MCH and TOL) solubility at elevated temperatures which in turn is caused by the larger entropic contribution at higher temperatures. The correlated UNIQUAC parameters are given in table 2.

### Table 2. Correlated UNIQUAC parameter for the MCH-toluene-Cyrene™ system

<table>
<thead>
<tr>
<th>Component ( i )</th>
<th>Component ( j )</th>
<th>( A_{ij} )</th>
<th>( A_{ji} )</th>
<th>( B_{ij} )</th>
<th>( B_{ji} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCH</td>
<td>Toluene</td>
<td>0</td>
<td>0</td>
<td>-191.0</td>
<td>171.5</td>
</tr>
<tr>
<td></td>
<td>Cyrene™</td>
<td>4.58 7</td>
<td>-2.627</td>
<td>-1749</td>
<td>773.7</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>2.70 8</td>
<td>-4.999</td>
<td>-772.6</td>
<td>1463</td>
</tr>
</tbody>
</table>

The LLX performance of Cyrene™ has been put in perspective by the comparison with other solvents, such as Sulfolane™, n-formylmorpholine²⁶, methanol²⁷ and various ILs, EMIM][ESO₄]⁴⁹, [HMIM][B(CN)₄]⁵⁰, [BMIM][B(CN)₄]⁵⁰ and [BMIM][MSO₄]⁵¹.
As can be seen in figure 3, Sulfolane™ is outperforming Cyrene™ regarding selectivity and n-formylmorpholine²⁶ has a higher selectivity at high toluene fractions in the solvent phase. Also, both solvents have a more significant phase split than Cyrene™. Comparable performance was seen towards methanol,²⁷ though Cyrene™ has a more significant phase split.

Figure 3. (left) A comparison of (left) the LLE and (right) $S_{\text{TOL,MCH}}$ at 298.15K of several solvents; Cyrene™, Sulfolane™, n-formylmorpholine²⁶, methanol²⁷, [EMIM][ESO₄]⁴⁹, [HMIM][B(CN)₄]⁵⁰, [BMIM][B(CN)₄]⁵⁰ and [BMIM][MSO₄]⁵¹. These systems were measured at 293.15K.

The ILs induce an almost complete immiscibility, due to lower distribution coefficients compared to traditional solvents. This immiscibility is due to their ionic nature, which
does not allow to stabilize in the highly apolar hydrocarbon mixture. Additionally, for low toluene fractions in the solvent phase, a similar selectivity towards toluene is observed for the ILs compared to Sulfolane™. Although, at higher toluene fraction the tetracyanoborate ILs⁵⁰ are able to retain a higher selectivity compared to Sulfolane™. A consequence of lower distribution coefficients in ILs is however that a larger solvent quantity is required for the LLX, and the equipment diameter will increase. On the other hand, due to the larger selectivity, less stages are required, reducing the equipment height. Higher selectivity means that less aliphatics need to be boiled from the solvent in the solvent regeneration, which is beneficial for the energy requirement, which seems to be in favor for ILs. Overall, it is not straight forward to decide which solvent is better and a more thorough process simulation including total annual cost estimation is suggested but outside the scope of this paper.

Methylcyclohexane – Cyclopentyl methyl ether - Cyrene™

As can be seen in figure 4, Cyrene™ induces a selectivity of 6.42±0.08, 4.55±0.41 and 3.91±0.31 at respectively 298.15K, 323.15K and 348.15K for ~0.65 wt. % of CPME in the solvent phase.
Figure 4. The ternary diagrams of the LLE of CPME, MCH and Cyrene\textsuperscript{TM} with the lie-lines, feed compositions and binodal curves at (a) 298.15K, (b) 323.15K and (c) 348.15K, and (d) the $S_{\text{CPME,MCH}}$ of Cyrene\textsuperscript{TM} at the same temperatures. The UNIQUAC fit is added throughout.
The results indicate that Cyrene™ is selective towards the polar ether moiety over the aliphatic MCH. A substantial miscibility region at CPME contents over ~35 wt. % CPME is observed, which resembles LLX-application window of the MCH-toluene case. In table 3, the UNIQUAC parameters of the correlation are displayed. This indicates that the dipolar characteristics of the ether moiety induces similar intermolecular interactions as the delocalized π-system of toluene.

Table 3. Correlated UNIQUAC parameter for the MCH-CPME-Cyrene™ system

<table>
<thead>
<tr>
<th>Component (i)</th>
<th>Component (j)</th>
<th>(A_{ij})</th>
<th>(A_{ji})</th>
<th>(B_{ij})</th>
<th>(B_{ji})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCH</td>
<td>CPME</td>
<td>0</td>
<td>0</td>
<td>-61.53</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>Cyrene™</td>
<td>3.33</td>
<td>2</td>
<td>-1356</td>
<td>588</td>
</tr>
<tr>
<td>CPME</td>
<td>2.31</td>
<td>-2.020</td>
<td>-661.0</td>
<td>899</td>
<td></td>
</tr>
</tbody>
</table>

Methylcyclohexane – Cyclohexanol – Cyrene™

The results for the system MCH – CHOH – Cyrene™ are given in figure 5. Cyrene™ induces a selectivity of 61.42±4.33, 32.8±5.83 and 16.6±2.26 at respectively 298.15K,
323.15K and 348.15K at ~0.80 wt. % of CHOH in the solvent phase. This is lower than observed with DMSO$^{36}$ and water$^{37}$, which have a selectivity of resp. 155 and 1450, at low CHOH concentrations.

The lower selectivity of Cyrene™ can mainly be attributed to the larger hydrocarbon backbone of Cyrene™, compared to the small DMSO and water molecules, which mitigates the multipole interactions with the relatively unselective London dispersion interactions.$^{52}$

Also in the ternary system MCH – CHOH – Cyrene™ a large miscibility region is observed, for concentrations above ~25 wt. % cyclohexanol. Due to the large miscibility in the system, only a small operation window is available for LLX, and the two phase region decreases at increasing temperature. The larger miscibility region indicates also that the capacity of Cyrene™ ($K_{D,\text{CHOH}} = 4.64$ at ~0.80 wt. % of CHOH in the solvent phase) for CHOH is larger than water ($K_{D,\text{CHOH}} = 1.60^{137}$).
Figure 5. The ternary diagrams of the LLE of cyclohexanol, MCH and Cyrene\textsuperscript{TM} with the tie-lines, feed compositions and binodal curves at (a) 298.15K, (b) 323.15K and (c) 348.15K, and (d) the $S_{\text{CPME,MCH}}$ of Cyrene\textsuperscript{TM} at the same temperatures. The UNIQUAC fit is added throughout.
Cyrene™ would be preferred when high CHOH capacities are required, while water is preferred when a larger immiscibility and selectivity is required. DMSO has been shown to be quite toxic and is for that reason not the preferred choice. The UNIQUAC parameters for this system are present in table 4.

**Table 4.** Correlated UNIQUAC parameter for the MCH-cyclohexanol-Cyrene™ system

<table>
<thead>
<tr>
<th>Component i</th>
<th>Component j</th>
<th>$A_{ij}$</th>
<th>$A_{ji}$</th>
<th>$B_{ij}$</th>
<th>$B_{ji}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCH</td>
<td>Cyclohexanol</td>
<td>-0.1112</td>
<td>-0.1675</td>
<td>-435.6</td>
<td>239.5</td>
</tr>
<tr>
<td></td>
<td>Cyrene™</td>
<td>-0.7045</td>
<td>-817.2</td>
<td>153.3</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td></td>
<td>0.7045</td>
<td>-128.7</td>
<td>12.0</td>
<td>5</td>
</tr>
</tbody>
</table>

**Methylcyclohexane – Cyclohexanone - Cyrene™**

The results for the ternary system MCH – CHO – Cyrene™ are given in figure 6. Cyrene™ induces a selectivity of 44.07±8.63, 32.14±2.78 and 19.25±2.00 at respectively 298.15K, 323.15K and 348.15K for the lowest amount of CHO in the solvent phase (~0.60 wt. %). Also in this case, the selectivity is lower than reported for DMSO and water, which have been reported to be 42.9 and 1202. Also in this case,
a significant miscibility region is observed at CHO contents higher than \(\sim 23\) wt. %. The single phase region is larger than compared to the previous systems, indicating a narrower LLX application window. This is due to the mutual presence of ketone functionality in CHO and Cyrene\textsuperscript{TM} resulting in a significant mutual solubility. Hence Cyrene\textsuperscript{TM} has a larger capacity for CHO \((K_{D,CHO} = 4.47\) at \(\sim 0.60\) wt. % of CHO in the solvent phase) than water \((K_{D,CHO} = 2.79^{1,37})\). Also for this case, Cyrene\textsuperscript{TM} and water may be preferred solvent choices, if either CHO capacity or immiscibly window and selectivity are the selection criteria. As previously mentioned, DMSO is toxic and is preferentially avoided. In table 5, the UNIQUAC parameters of the correlation are displayed.
Figure 6. The ternary diagrams of the LLE of cyclohexanone, MCH and Cyrene\textsuperscript{TM} with the tie-lines, feed compositions and binodal curves at (a) 298.15K, (b) 323.15K and (c) 348.15K, and (d) the $S_{CPME,MCH}$ of Cyrene\textsuperscript{TM} at the same temperatures. The UNIQUAC fit is added throughout.
Table 5. Correlated UNIQUAC parameter for the MCH-cyclohexanone-Cyrene™ system

<table>
<thead>
<tr>
<th>Component i</th>
<th>Component j</th>
<th>A_{ij}</th>
<th>A_{ji}</th>
<th>B_{ij}</th>
<th>B_{ji}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCH</td>
<td>Cyclohexanone</td>
<td>-1,090</td>
<td>-1,090</td>
<td>364,9</td>
<td>364,9</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>MCH</td>
<td>4,587</td>
<td>-2,627</td>
<td>-1749</td>
<td>773,7</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>Cyrene™</td>
<td>2,507</td>
<td>-7,521</td>
<td>-531,6</td>
<td>2133</td>
</tr>
</tbody>
</table>

Comparative Study

By considering the combined data from all ternary systems with toluene (TOL), cyclohexanol (CHOH), cyclohexanone (CHO) and CPME, from MCH, the performance of Cyrene™ towards particular moieties can be evaluated. Cyrene™ is a bi-cyclic organic molecule in which a double ether moiety, one in each ring, and a ketone functionality is present. All moieties are aprotic and therefore can only act as a hydrogen bond acceptor and will induce next to the omnipresent London dispersion interactions also Keesom and Debye interactions.\textsuperscript{52} Comparing the results, see table 6 and from the figures 2, 4, 5 and 6, it is concluded that selectivity order is found to be mostly CHO\textsubscript{H} > CHO   ≫ TOL > CPME. A larger temperature-dependency is seen for
CHOH, likely due to intra- and intermolecular hydrogen bonding, resulting in lower selectivity than CHO at higher temperatures.

Table 6. A comparison between the distribution coefficient and selectivity found for CHOH, CHO, TOL and CPME at similar low weight percentage in the solvent phase at 298.15K, 323.15K and 348.15K

<table>
<thead>
<tr>
<th>Component</th>
<th>Component</th>
<th>Component j in solvent phase (wt.%)</th>
<th>Distribution Coefficient component j (-)</th>
<th>Selectivity (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>j</td>
<td></td>
<td>(298.15K / 323.15K / 348.15K)</td>
<td></td>
</tr>
<tr>
<td>MCH</td>
<td>CHOH</td>
<td>0.80 / 0.65 / 0.51</td>
<td>4.64 / 2.94 / 1.64</td>
<td>61.4 / 32.8 / 16.6</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>0.87 / 0.60 / 0.56</td>
<td>4.47 / 3.15 / 2.20</td>
<td>44.1 / 32.1 / 19.3</td>
</tr>
<tr>
<td></td>
<td>TOL</td>
<td>0.74 / 0.82 / 0.72</td>
<td>0.98 / 0.54 / 0.51</td>
<td>12.0 / 5.80 / 5.32</td>
</tr>
<tr>
<td></td>
<td>CPME</td>
<td>0.83 / 0.63 / 0.57</td>
<td>0.30 / 0.40 / 0.40</td>
<td>5.15 / 4.27 / 3.54</td>
</tr>
</tbody>
</table>

CHOH and CHO are extracted with significantly higher selectivity than toluene and CPME. This is due to respectively the hydrogen bond donating character of CHOH and the significant dipole moment of 2.75D\textsuperscript{54} of CHO which induces substantial Keesom and Debye interactions with Cyrene\textsuperscript{TM}. Toluene and CPME do not have hydrogen bonding donating capabilities and have much lower dipole moments compared to
CHO, respectively 0.37D\textsuperscript{55} and 1.27D\textsuperscript{56}, hence a lower selectivity is induced. Toluene does however exhibit a significant quadrupole moment,\textsuperscript{57} which is responsible for more extensive Keesom and Debye interactions and therefore a larger selectivity is induced compared to CPME.

When the CHO and CHOH cases are combined and their extraction performances are compared, a measure of selectivity towards both solutes may be estimated for the lowest weight fractions of solute in the solvent phase. A selectivity ratio (S_{\text{CHOH,MCH}}/S_{\text{CHO,MCH}}) of 1.42 and 1.21\textsuperscript{37} is obtained for resp. Cyrene\textsuperscript{TM} and water. We speculate that Cyrene\textsuperscript{TM} is a slightly more selective solvent for the combined extraction of CHO and CHOH than water, though this may be caused by the different alkane used in both studies. A Cyrene\textsuperscript{TM}-based LLX process for this separation was further investigated by short-cut energy calculations in the next section.

**Process Considerations**

Liquid-Liquid Equilibria are cornerstones in an accurate description of Liquid-Liquid Extractions (LLX) that arguably form the heart of LLX processes. As solvents are rarely completely immiscible and selective, several additional purification steps are required
to recover the solvent and obtain a pure product. An example is given by an de Graff et al.\textsuperscript{58} where two distillation columns are used to recover the solvent and pure products from a LLX column. The raffinate can also be distilled to recovery the solvent, though for polar solvents the use of a water wash column to recover the solvent can be applied to save energy. Subsequently, the water is then evaporated from the solvent-rich water phase and the vapor is used to strip extracted solutes from the extract stream.\textsuperscript{59-61} To thoroughly compare Cyrene™ with all conventional solvents for all studied applications will require rigorous process simulations for all these process steps, and even consideration on which of the steps are required and preferred. This is beyond the scope of this paper, in which the applicability of Cyrene™ is explored and a first indication of the usefulness of the application is discussed on the basis of miscibility, distribution coefficients and selectivity. On the basis of a short-cut calculation an estimation of the required heat duty will be given for the combined case of MCH/CHO and MCH/CHOH. This case was chosen as being most interesting for industrial application in the industrial oxidation process of cyclohexane to CHO and CHOH\textsuperscript{34-35}. The MCH-TOL case which certainly is also of industrial interest was not simulated because on the basis of the liquid-liquid equilibrium data it can be seen that both
Sulfolane and ILs are clearly superior over Cyrene™ with regard to selectivity and immiscibility.

The most significant difference between water and Cyrene™ is related to the recovery of the CHO and CHOH from the solvent, which boil at resp. 429K and 433K. Cyrene™ is a high-boiling solvent (bp: 500K), whereas water is a low-boiling solvent (bp: 373K). Recovery of water thus implies that the solvent has to be boiled off from the solutes, whereas the solutes can be boiled off from the Cyrene™. Cyrene™ has therefore a significant advantage over water, due to the fact the energy-penalty associated with the evaporation enthalpy of the solvent is avoided in using the high-boiling Cyrene™. Also, the capacity of CHO and CHOH in water is lower compared to Cyrene™. This entails a larger amount of water is required to extract a certain amount of CHO and/or CHOH than Cyrene™.

In order to estimate the magnitude of the energy advantage, a set of rough calculations on the heat duty in the recovery processes were performed. Using the LLE description by UNIFAC, the minimum solvent to feed (S:F) ratio (on mass basis) was determined by simulation in ASPEN Plus of the LLX process with 1000 equilibrium stages, a feed containing 90 wt. % MCH, and obtaining >99.9 wt. % MCH purity.
Afterwards, for the heat duty in the solvent recovery stage, a short-cut calculation was applied. Assuming that most of the sensible heat may be recoverable using heat exchangers, the latent heat of vaporization ($\Delta H_{vap}$) of the most volatile compound was used as estimate. For water as solvent, a minimum S:F ratio of 1.8 was obtained for CHOH and 7.3 for CHO. Since water for these systems is a volatile solvent, evaporation of all the water resulted in a heat duty of 41.3 MJ/kg$_{\text{CHOH}}$ and 166 MJ/kg$_{\text{CHO}}$.

For Cyrene™, a lower minimum S:F ratio was required which is a direct consequence from the larger capacity towards CHO and CHOH, being 1.2 for CHOH and CHO. Furthermore, since Cyrene™ in these systems is a high boiling solvent, the solutes CHOH and CHO should be boiled off. Due to solvent leaching, MCH should be boiled off from the raffinate to recover the solvent, and the evaporation of MCH from the raffinate is included in the calculations. This resulted for CHOH in a heat duty of 3.86 MJ/kg$_{\text{CHOH}}$ and for CHO in 3.87 MJ/kg$_{\text{CHO}}$. These short-cut calculations show that extraction processes using Cyrene™ instead of water may be 11 times more efficient for the separation of CHOH from MCH and 43 times more efficient for CHO from MCH. This is a rough heat duty estimate, and in an accurate process simulation, the final
heat duty may be less beneficial. However, with the current figures, it shows high potential for a significant advantage of the high boiling Cyrene™ over the low boiling water. The fact that most energy savings compared to water were accomplished by the higher boiling point of the solvent, suggests that for this application the use of ionic liquids (ILs) might be interesting too, on the condition that beneficial behavior is observed in LLE. However, no LLE data has been found for MCH/CHOH or CHO with an IL.

The separation of CHO and CHOH may also be accomplished with Cyrene™ due to the fact a larger selectivity is observed toward CHOH than CHO. Although no phase separation is expected and LLX is not possible, other separation techniques may be used such as extractive distillation or perhaps with a extractive divided wall configuration.

**Conclusion**

Four biphasic ternary systems have been assessed in which methylcyclohexane (MCH) and Cyrene™ were kept constant. As third compound toluene, cyclohexanol, cyclohexanone and cyclopentyl methyl ether (CPME) were applied. For each ternary
system a selective extraction was found at the three studied temperatures of 298.15K, 323.15K and 348.15K. Cyclohexanol (up to $S_{\text{CHOH,MCH}} = 61.42 \pm 4.33$) and cyclohexanone (up to $S_{\text{CHO,MCH}} = 44.07 \pm 8.63$) were most selectively extracted, while toluene (up to $S_{\text{TOL,MCH}} = 11.99 \pm 0.89$) and CPME (up to $S_{\text{CPME,MCH}} = 6.42 \pm 0.08$) were extracted with considerably lower selectivity. While Cyrene™ was outperformed by Sulfolane™ and several ionic liquids in the extraction of toluene, the potential of Cyrene™ in the cyclohexanol/cyclohexanone systems was observed. Although a lower selectivity was seen than with water, due to the high boiling point of Cyrene™, recovery can be much less costly. Overall, we conclude that Cyrene™ can be applied as biobased extraction solvent for a variety of separations, although for several systems the phase envelop is relatively narrow and narrower at higher temperatures.

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Supporting Information

Electronic Supporting Information is available online, and contains four tables with all experimental data for figures 2, 4, 5 and 6, including weight percentages of all
compounds in each phase, the distribution coefficient of MCH and the solute (being TOL, CHO, CHOH or CPME), and the selectivity of that solute over MCH. The thermodynamic consistency of all UNIQUAC correlations was checked using the determinant of the Hessian matrix approach, and the results displayed in four figures.

Abbreviations

\[ [\text{BMIM}][\text{B(CN)}_4] \] - 1-butyl-3-methylimidazolium tetracyanoborate

\[ [\text{BMIM}][\text{MSO}_4] \] - 1-butyl-3-methylimidazolium methylsulfate

\[ [\text{EMIM}][\text{ESO}_4] \] - 1-ethyl-3-methylimidazolium ethylsulfate

\[ [\text{HMIM}][\text{B(CN)}_4] \] - 1-hexyl-3-methylimidazolium tetracyanoborate

\[ X_i^O \] - Weight Fraction of compound i in the organic phase

\[ X_i^S \] - Weight Fraction of compound i in the solvent phase

\[ A_{ij} \] - Temperature independent UNIQUAC fit parameter

\[ B_{ij} \] - Temperature dependent UNIQUAC fit parameter

\[ B_p \] - boiling point

\[ \text{CHO} \] - Cyclohexanone

\[ \text{CHOH} \] - Cyclohexanol

\[ \text{CPME} \] - Cyclopentyl methyl ether

\[ \text{Cyrene}^{\text{TM}} \] - Dihydrolevoglycosenone

\[ D \] - Debye
DMF - N,N-dimethylformamide
DMSO - Dimethylsulfoxide
ED - Extractive Distillation
$K_{D,i}$ - Distribution coefficient of solute i
LLE - Liquid-liquid equilibrium
LLX - Liquid-liquid extraction
MCH - Methylcyclohexane
NMP - N-methylpyrrolidone
$q_i$ - Van der Waals surface area of solute i
$r_i$ - Van der Waals volume of solute i
$S_{ij}$ - Selectivity of solute i over solute j
Sulfolane™ - Tetrahydrothiophene-1,1-dioxide
SI - Supporting Information
S:F ratio - Solvent to Feed ratio (mass basis)
T(K) - Absolute temperature
TOL - Toluene
UNIQUAC - Universal Quasichemical
$y_i$ - Activity Coefficient of solute i
$y_i^c$ - Combinatorial term of the activity Coefficient of solute i
$y_i^R$ - Residual term of activity Coefficient of solute i
$\phi_i$ - volume fraction
$\theta_i$ - surface area fraction
\[ \tau_{ij} \] - binary interaction parameter between solutes i and j

- Extrapolated from corresponding literature to similar solute concentration in solvent phase.

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Cyrene™ extracts solutes more polar than methylcyclohexane selectively from the hydrocarbon phase.