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Full-length article

Rational solvent selection for the preparation of industrial monolithic supported liquid-phase (SLP) olefin hydroformylation catalyst

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ABSTRACT

Heterogenisation of the hydroformylation (HyFo) process converting C4 olefins and syngas (CO/H₂) to *n*-pentanal can substantially reduce its carbon footprint by simplifying downstream processing. Current upscaling efforts include constructing a pilot plant containing a Rh-diphosphite-stabilized supported liquid-phase (SLP) catalyst. The air-sensitive nature of the catalyst requires *in-situ* impregnation of the porous support material with the liquid phase components (Rh-precursor, ligand, stabiliser) entailing the use of large quantities of an organic solvent. Environment, health, and safety (EHS) as well as regulatory aspects prompt the search for an alternative to dichloromethane (DCM), which was used as standard solvent for lab-scale studies. To obtain alternatives to DCM, the replacement solvent methyl *tert*-butyl ether (MTBE) and *in-silico* screening of more than 5000 solvent candidates has been performed covering boiling points and solubility predictions by COSMO-RS as well as carcinogenicity- and mutagenicity predictions by quantitative structure–activity relationship (QSAR) models. The final list of solvent candidates contained unsaturated compounds (alkenes, alkynes) in addition to ether- and ester-functionalized solvents, which are typically recommended as DCM replacements. Sufficiently high solubilities of ligand and stabiliser to prepare the desired SLP catalyst were experimentally determined in the following solvents: methyl propionate (MP), dimethoxymethane (DMM), MTBE, tetrahydrofuran (THF) and DCM for benchmarking, and a monolithic SLP catalyst prepared with MTBE demonstrated to perform equally well in the HyFo reaction of 1-butene as the benchmark catalyst prepared using DCM solvent. Overall, the study demonstrates a practical approach for selecting solvents with a greener profile for making catalyst systems applicable for large-scale production.

1. Introduction

Catalysis is the cornerstone technology that makes it technically, economically, and ecologically possible to produce practically all the chemical products utilized in our modern industrialized world. One of the most prominent examples of industrial application of homogeneous catalysis is hydroformylation (HyFo), where olefins react with syngas (CO/H₂ gas mixture) yielding aldehydes [1,2]. The annual production volume of HyFo is nowadays more than 12 million tons with *n*-pentanal as one of the major aldehydes produced [3]. Notably, the demand for *n*-pentanal is expected to further increase in the coming years as it is a precursor for 2-propyl-heptanol (2-PH), which is a next-generation plasticizer alcohol [4,5]. In addition, 2-PH can be used in a wide range of special applications in plastic and surfactant value chains.

The homogeneously catalyzed HyFo process for *n*-pentanal production utilizes typically a Rh-complex catalyst coordinated to a diphosphite ligand such as for example biphephos (bpp) [4]. Bpp allows the

use of economical raffinate feedstocks [1,4,6,7] rich in 2-butene by facilitating an isomerization-HyFo tandem reaction (Fig. 1) and affords excellent regioselectivity of the desired linear aldehyde product (*n*-pentanal) compared to the *iso*-aldehyde product (2-methylbutanal) [4,7]. However, as with other homogeneously catalyzed processes separation of the product from the liquid catalyst phase entails high energy consumption [6,8]. Therefore, novel reaction systems aimed at facilitating separation have been extensively studied [6,9–11] and especially heterogenisation of the Rh-complex based catalyst has shown great potential in the gas-phase hydroformylation of C4 feedstocks.

One of the most promising HyFo heterogenisation strategies is to use supported liquid-phase (SLP) systems, where the Rh-bpp catalyst is dissolved in a liquid phase having negligible vapour pressure which is located in the pores of a solid support [6,7,12–14]. Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (hereafter abbreviated as sebacate) has proved to be an auspicious liquid phase for C4 gas-phase HyFo

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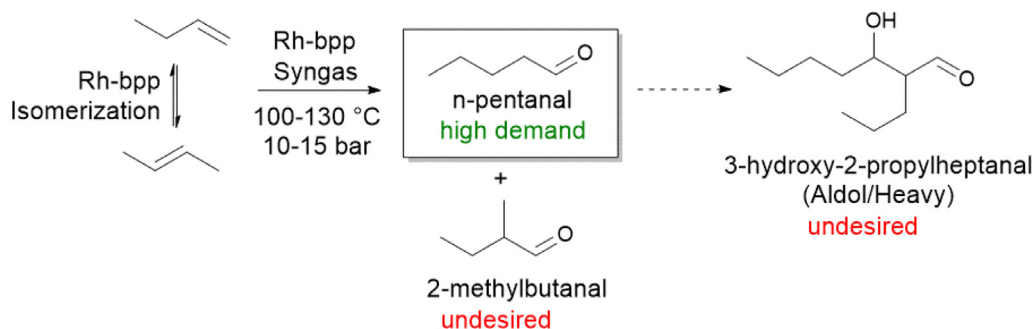


Fig. 1. Reaction network for the HyFo reaction using C4 raffinate.

at the process temperature of 100-130 °C. A moderate solubility of *n*-pentanal in sebacate strongly suppresses the unwanted consecutive aldol condensation reaction (Fig. 1), which yields high boiling compounds that can accumulate in the pore system and cause strong reduction of the catalytic activity [6,12,15,16].

Based on promising bench scale results obtained with the Rh-bpp-sebacate SLP system, long-term operation of a demonstration plant (TRL 7) is currently ongoing [17,18] using a SiC monolithic support material having high mechanical- and chemical resistance as well as good thermal conductivity and multimodal pore size distribution [14,19]. In addition, the cylindrical monoliths can be coated with a polymeric membrane allowing selective *in-situ* aldehyde separation and hereby further suppress formation of high-boiling aldol products [12,20].

During the preparation of the monolithic Rh-bpp-sebacate SLP system, the three catalyst components are introduced to the pore system of the support by impregnation [12,13] using a stock solution of the components dissolved in a suitable solvent. The molecular structures of each component in the SLP catalyst system as well as their chemical incompatibilities and concentrations in stock solutions are compiled in Fig. 2. The impregnation procedure needs to be performed at minimum water and oxygen concentrations due to the sensitivity of the ligand [21,22]. Likewise, air exposure of the catalyst in between solvent removal and reaction start-up should be avoided, thus making *in-situ* impregnation in the reactor a desirable option, as depicted in SI Fig. S1. The *in-situ* impregnation also allows for re-coating of the support without dismantling of the reactor, leading to greater flexibility and the possibility of re-activation of the system. For the bench scale impregnations, dichloromethane (DCM) was the solvent of choice due to obvious merits like excellent solvating power for bpp and ease of removal due to its low boiling point (bp 39.6 °C). However, DCM is suspected to be carcinogenic to humans and has been shown to be ozone depleting [23]. This makes it incompatible with process upscaling in industrial settings having increased demands on environment, health, and safety (EHS) as well as regulatory aspects, including the choice of impregnation solvent.

Solvent selection has received increasing attention in industry due to the related life cycle and EHS impacts [23–27], and several companies have published solvent selection guides (SSGs) [25,27–31] and reviews on the guides [23,32,33]. The SSGs typically contain simple guidelines for experimental chemists and group solvents into three categories. For example, Pfizer [23] uses the categories “preferred”, “usable” and “undesirable” and gives a solvent replacement table for the “undesirable” ones, e.g. alternatives for DCM in extractions are ethyl acetate, methyl *tert*-butyl ether (MTBE), toluene and 2-methyltetrahydrofuran (Me-THF). Due to their user friendliness and simplicity, SSGs have been widely adopted by industrial chemists leading to significant improvements in solvent-related EHS impacts [23]. For the herein described DCM replacement case, MTBE was indeed the most obvious choice due to easy access of the solvent in bulk quantity near the demonstration plant without further regulatory work necessary for its use at the plant site. However, to future-proof the *in-situ* impregnation, especially regarding potential needs to increase the

solutes’ concentrations and regulatory changes pertaining the use of MTBE, additional solvent alternatives were also pursued.

To allow for a more holistic solvent selection framework, later versions of SSGs [30] also include *principal component analysis* (PCA) data and *cosmo* files associated with the COSMOtherm [34] package. These expansions help to search for solvents with specific physicochemical properties that also comply with EHS demands. A collaboration between the American Chemical Society (ACS) and the pharmaceutical industry led to the introduction of a user-friendly web-based freeware [35] covering 272 solvents though not including the *cosmo* files. While this tool allows to screen solvents on a multitude of physicochemical properties such as boiling point and presence of functional groups, it has shortcomings regarding solubility predictions as only solubility parameters such as Hansen parameters are included [36]. These allow finding solvents expected to have similar solubilizing power to a given solvent (e.g., DCM) but do not necessarily find the best ones for a given set of solutes. Another useful freeware tool with special focus on the environmental and health impacts of solvents is the PARIS III (Program for Assisting the Replacement of Industrial Solvents III) package [37]. While it enables the search for solvents through eight physical properties and the solvents’ interaction with solutes from ten chemical families in the form of infinite dilution activity coefficients, it too does not allow for solute specific solubility predictions. COSMO-RS calculations on the other hand can generate solubility rankings for each solute [38]. EHS indicators such as carcinogenicity and mutagenicity can likewise be rapidly predicted using quantitative structure–activity relationship (QSAR) models implemented in, e.g. the VEGA HUB suite [39]. Also, solubility predictions by COSMO-RS of solvent pools pre-screened by PARIS III for EHS factors have recently been reported [40,41].

In this work, an *in-silico* solvent screening of more than 5600 candidates has been completed to find further industrially viable impregnation solvents for the Rh-bpp-sebacate SLP catalyst system using a pre-existing *cosmo* files database and EHS indicators. Furthermore, the solubilities of bpp and sebacate were measured experimentally in two of the final solvent candidates as well as in DCM, MTBE and THF (overall workflow shown in SI Fig. S2). Finally, a monolithic SiC support was impregnated with the Rh-bpp-sebacate catalyst system using the industrially most practical solvent candidate (MTBE), and the resulting SLP catalyst performance was tested against a DCM impregnated SLP catalysts in the HyFo reaction of 1-butene.

2. Materials and methods

2.1. Solubility and boiling point predictions

Solubility predictions of the catalyst components Rh(acac)(CO)₂, bpp and sebacate in various solvents were based on the inverse of the activity coefficients at infinite dilution, which were calculated using the COSMO-RS method [34,42–44] with the BP_TZVP parametrization. The compounds and their COSMO charges were taken from the COSMObase

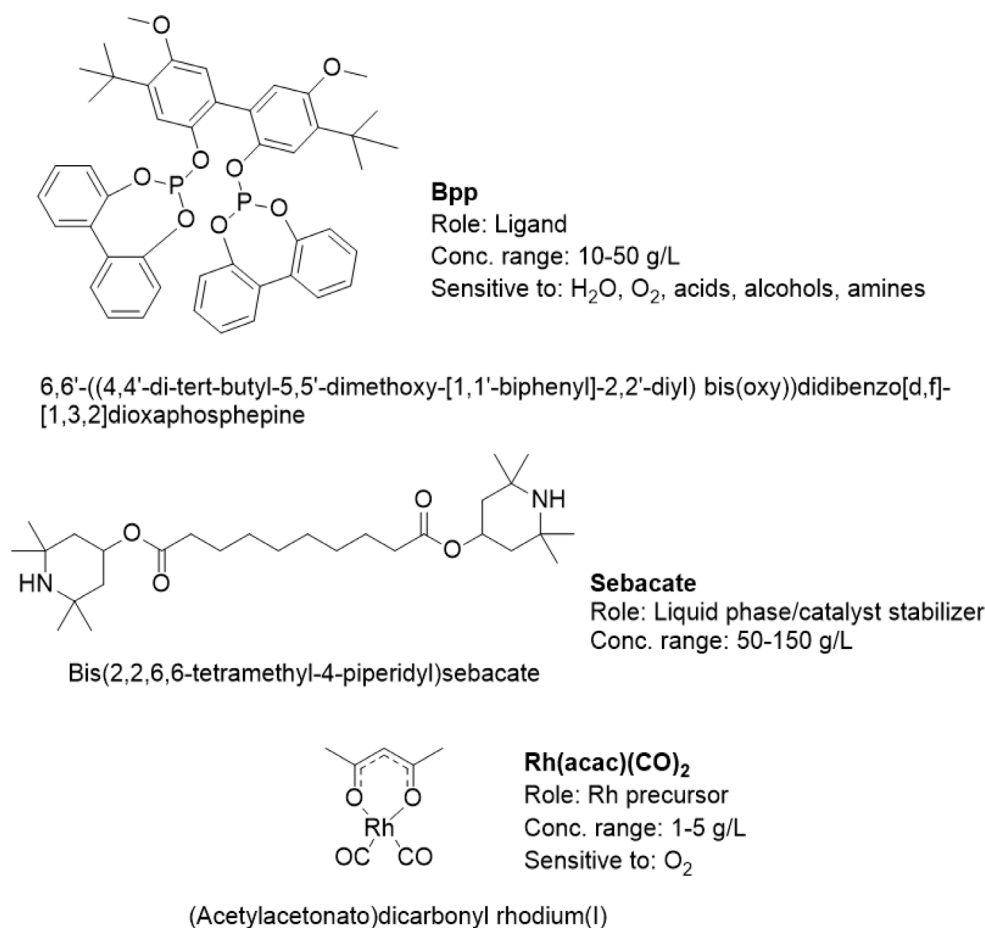


Fig. 2. Components of the C4 HyFo SLP catalyst system including their role, concentration range in stock solution and chemical incompatibilities.

database [45] without any pre-filtering. For compounds not available in the database, their COSMO charges were calculated using the quantum chemistry package TURBOMOLE [46]. The database COSMObase also contains experimental boiling points for a subset of substances. For these substances, the experimental boiling points were used. For the remaining substances, the boiling points were estimated using COSMO-RS [34,42–44]. The activity coefficients of the three solutes (γ_{solute}) were multiplied by their relative mass-based abundance reflecting a Rh:bpp:sebacate molar ratio of 1:4:16 to account for the vastly different solubility requirements (see Fig. 2). The solvent ranking was performed according to Eq. (1) with a lower rank suggesting a more suitable solvent. Only solvents with a lower rank than ethyl acetate were considered, as this solvent, according to Eq. (1), is the worst ranked of the common DCM replacements.

$$\text{Rank} = \text{Min}(\text{Max}(\gamma_{\text{Rh}(\text{acac})(\text{CO})_2} \times 1; \gamma_{\text{bpp}} \times 12.2; \gamma_{\text{sebacate}} \times 29.8)) \quad (1)$$

2.2. EHS indicator predictions

Computer Assisted Evaluation of industrial Chemical Substances According to Regulations (CAESAR) models v.2.1.9 and v.2.1.13 as implemented in VEGA HUB [47] were used to predict carcinogenicity and mutagenicity, respectively. The required Simplified Molecular-Input Line-Entry System (SMILES) molecular representations were generated as shown in SI Fig. S3. From the final list of solvents after the solubility screening, all candidates with hazard symbols other than “flammable” (flame) and “irritant” (exclamation mark) as well as those containing certain functional groups such as, e.g. halogens (see Table 1) were excluded.

2.3. Solubility measurements

Solubilities of bpp and sebacate were experimentally determined in selected solvents by preparing saturated solutions of the components with 1:4 molar ratios of bpp:sebacate. The obtained mixtures were vigorously stirred at 25 °C overnight under inert argon atmosphere. The stirring was then stopped, and the solution settled for 1–2 h to allow complete separation of supernatant from the precipitate. Then, 0.5 mL of supernatant was analysed for sebacate and bpp by ¹H and ³¹P nuclear magnetic resonance (NMR) spectroscopy (25 °C, 400 MHz, Bruker Ascend 400 MHz spectrometer, reference to D₂O).

2.4. Preparation of SLP catalysts

Monolithic tubular SiC supports (200 mm × 25.4 mm, 30 channels of 3 mm diameter, LiqTech) [13] were impregnated under argon atmosphere with stock solutions based on MTBE (99.8%, Sigma-Aldrich) and DCM (99.8%, Sigma-Aldrich) containing 51.5 mg Rh(acac)(CO)₂ (98%, Sigma-Aldrich), 627 mg 6,6'-[(3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)bis(oxy)]-bis(di-benzo[d,f] [1–3]-dioxaphosphepine) (bpp, Evonik Oxeno GmbH) and 1.533 g bis(2,2,6,6-tetramethyl-1,4-piperidyl)sebacate (sebacate, Evonik Oxeno GmbH), respectively. The stock solution was added dropwise to the top of the monolith in vertical position. After drainage of excess stock solution, drying was performed for about 2 h in a flow of argon followed by vacuum (~1 mbar) until no more weight loss was observed.

2.5. HyFo catalysis with SLP catalysts

The prepared monolithic SLP catalysts were tested in continuous, gas-phase HyFo of 1-butene at 110 °C and 10 bar(a) pressure for 50 h

Table 1
Prominence of selected functional groups and numbers of solvents after screening filters.

Functional group	<i>In-silico</i> filter (%) ^a			Manual filter (%) ^b
	Boiling point	Carcinogens and mutagens	Solubility	
Halogen	25.6	15.2	16.1	–
Ether	12.9	18.3	18.8	50.0
Ester	6.2	8.0	15.2	23.1
Ketone	3.9	3.1	2.7	–
Aldehyde	3.8	2.2	2.7	–
Amine	8.4	17.0	26.8	–
Amide	0.5	1.9	–	–
Pyridine	1.1	1.9	–	–
Thiol	1.8	2.5	6.3	–
Aromatic	5.5	10.5	10.7	11.5
Alkene	18.2	14.9	9.8	15.4
Alkyne	4.5	3.7	3.6	7.7
Alcohol	6.5	3.7	2.7	–
Number of solvents	1327	323	112	26

^a Accepted experimental boiling point: 35–110 °C; Hazard symbols accepted: “flammable” and “irritant”. Solubility accepted: More favourable than ethyl acetate according to Eq. (1).

^b Functional groups discarded: Halogens (safety and environmental concerns), amines (potentially attack the ligand), alcohols (attack the ligand), carboxylic acids (attack the ligand), organoaluminium compounds (react violently with moisture), nitrates (potentially attack the ligand), silanes (expensive), and isocyanates (too reactive).

time on stream (TOS) in a test-rig as shown in SI Fig. S4. Further details on the testing conditions and analytics are also provided in the SI, including Table S1.

3. Results and discussion

3.1. *In-silico* solvent screening

Table 1 shows the prominence of selected functional groups of the solvents after applying *in-silico* filters for boiling point, carcinogens and mutagens, as well as finally solubility of the catalyst components. Halogen atoms were present in about a quarter of the compounds (25.6%) after application of the boiling point filter to the initial database, making it the most common functional group at that stage. Filtering for predicted carcinogens and mutagens removed an over proportional share of halogenated solvents, almost halving their relative incidence (15.2%), which is not surprising due to the relevant, documented risks of some halogenated solvents including DCM [48–52]. After the solubility filter, halogens were strongly represented (16.1%) in line with previous knowledge of halogenated solvents having strong solubilization power for the Rh-bpp catalyst as well as in the case of DCM for the Rh-bpp-sebacate system [12,53]. Ethers were also strongly represented at all stages and their share increased by filtering out suspected carcinogenic and mutagenic solvents (18.8%). The relative benignity of ethers and their solubilizing properties being quite similar to DCM also align with the fact that SSGs propose two ethers, namely Me-THF and MTBE, among the few replacement options [28,31,32]. Unexpectedly, however, in the current study MTBE was predicted to be carcinogenic and hence did not make it into the final list of solvent candidates.

Ester functionality was present in 17 out of the 112 (15.2%) post-solubility filter solvent candidates. However, the commonly proposed DCM replacement ethyl acetate, just like MTBE, had to be discarded on the grounds of predicted carcinogenicity. Notably, both amine- and thiol-based solvents had a surprisingly strong representation among the final candidates, but, like alcohols, they can degrade phosphite ligands by nucleophilic attack [54,55] and were accordingly also discarded. A total of 11 aromatic solvents were among the final candidate list of which 8 contained a phenyl ring and 3 a furan system. As all the former compounds also contained halogen atoms, they were not considered beyond the *in-silico* screening. Other functional groups discarded for the solvents included carboxylic acids, organoaluminum compounds, nitrates, silanes, and isocyanates.

The initial *in-silico* screening and the removal of solvents with incompatible functional groups resulted in 47 remaining solvent candidates (see list in SI Table S2). Further manual filtering was first based on acceptable experimental boiling points (35–110 °C) allowing relatively low-energy removal by evaporation. Note that solvents with boiling points in the lower end of this range would not be applicable at elevated ambient temperatures, e.g. during summertime, because high vapour pressure would complicate solvent handling. The catalyst components are known to be stable at the higher end of the temperature range [15]. After filtering by hazard symbols as described in Table 1, a final of 26 solvent candidates remained which were heavily dominated by ethers (50.0%) followed by esters (23.1%) and alkenes (15.4%). While the strong presence of the former two groups was not surprising and some candidates might have been proposed based on chemical intuition, the resulting alkenes and alkynes such as 3,3-dimethyl-1-butyne, 3-methyl-3-penten-1-yne and 3-methyl-1,4-pentadiene were less obvious and demonstrate how *in-silico* screening methods can widen the relevant chemical space.

3.2. Experimental solubilities

From the list of potential solvents resulting from the screening procedure were two candidates (one ether and one ester) selected for further experimental solubility investigations. DMM was chosen based on its favourable boiling point (41 °C) and its widespread industrial usage [56,57], whereas the even lower boiling point of diethyl ether (35 °C) was seen as a disadvantage as it complicates solvent handling. MP was selected as an ester candidate due to its relatively low boiling point (78 °C) and ready availability [58]. Moreover, even though not being on the final list, MTBE was also evaluated as it does not require further regulatory work to implement at the demonstration plant premises as mentioned above. In addition, a recent critical review concluded based on the integration of exposure, toxicologic (including genotoxicity) and toxicokinetic evidence, that the cancer risks of MTBE to humans are minimal [59]. Therefore, the predicted carcinogenicity by CAESAR model v.2.1.9 is probably a false positive. Finally, THF was also investigated as it is a standard solvent previously used for Rh-bpp catalyzed HyFo systems [60,61]. Solubilities in DCM served as benchmark.

Fig. 3 shows the experimentally measured solubilities of bpp and sebacate at 25 °C from both single- and double component systems as a function of the inverse activity coefficient ($1/\gamma_{\text{solute}}$) obtained from COSMO-RS calculations. Bpp exhibited generally lower solubility than sebacate in all solvents, except for DCM where an extraordinary high solubility well above the design range (10–50 g/L) was found, both

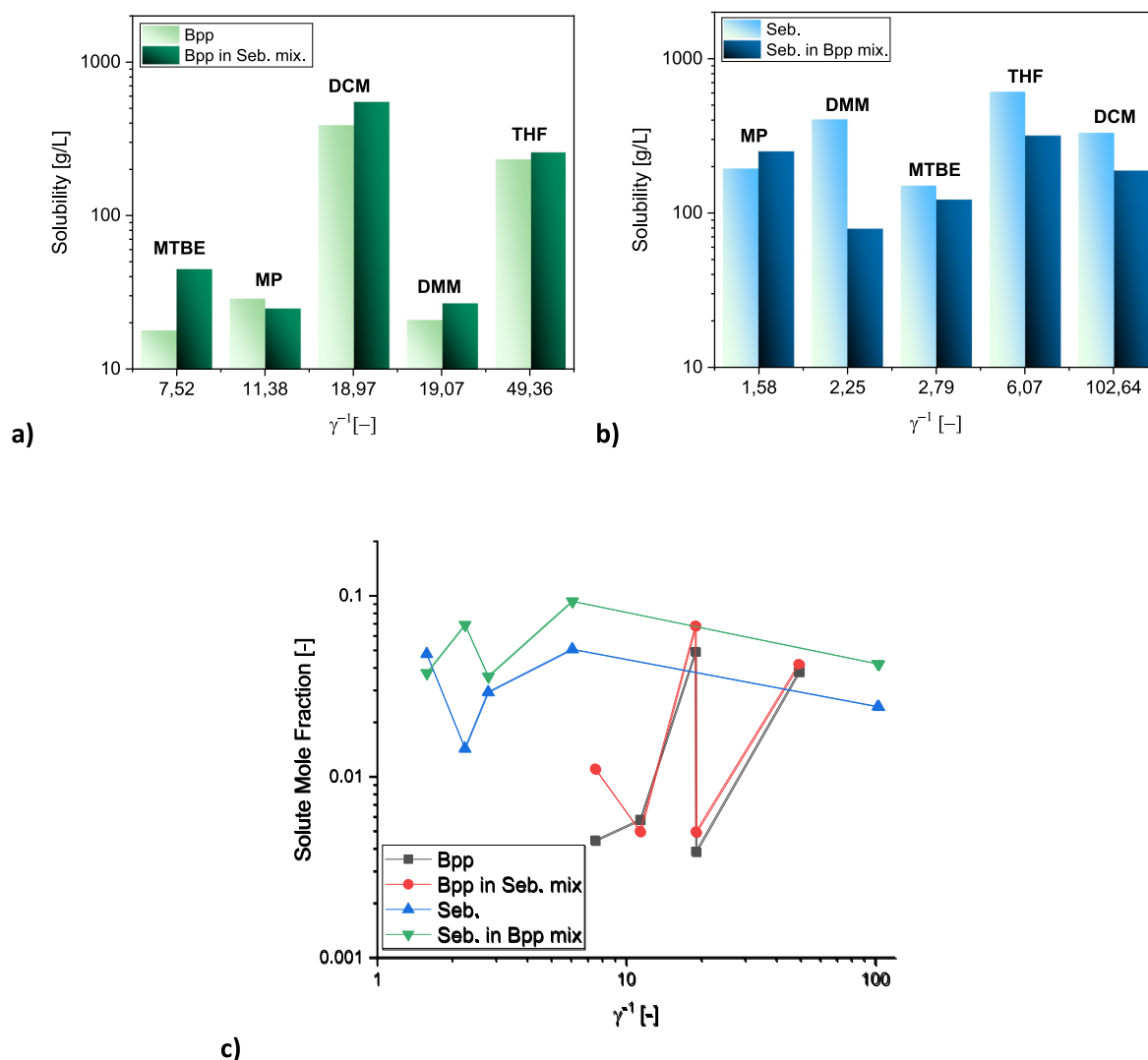


Fig. 3. Experimentally obtained solubilities (a and b) and molar fractions (c) as function of predicted activity coefficients. Double component systems derived from seb:bp mixtures with 1:4 molar ratios. MTBE: methyl *tert*-butyl ether, MP: methyl propionate, DCM: dichloromethane, DMM: dimethoxymethane, THF: tetrahydrofuran.

in the presence and absence of sebacate. In contrast to MTBE, MP, and DMM afforded bpp single component solubilities, which were only in the middle of the design range (19.5–28.9 g/L). Interestingly, the presence of sebacate slightly decreased the bpp solubility in MP but increased the solubility markedly by >100% in MTBE (from 19.5 to 45.0 g/L). This synergistic effect reflects the ability of molten sebacate to dissolve bpp under operating conditions of the HyFo reaction. The MTBE-based binary solution also contained sebacate (122 g/L) in the higher end of the design range. On the other hand, as only modest amounts of bpp was dissolved in binary systems with MP (24.5 g/L) and DMM (26.9 g/L) the bpp loadings (and Rh loadings) needs to be adjusted to uphold the set molar Rh:bp:sebacate ratio of 1:4:16 if using these solvents for catalyst preparation.

All the investigated solvents showed high single component sebacate solubilities at or above the limit of the design range (150 g/L). Furthermore, the presence of bpp slightly increased the solubility of sebacate in MP, while the solubility in contrast was decreased slightly in MTBE and more markedly in THF, DCM, and DMM. Nevertheless, despite DMM had lower simultaneous solubility of bpp (26.9 g/L) and sebacate (78.6 g/L), the concentrations remained 35 and 57% higher, respectively, than the ones used in the previously reported Rh-bpp-sebacate SLP system [12]. Noticeably, THF could simultaneously accommodate bpp (258 g/L) and sebacate (316 g/L) at very high

concentrations. This may inspire to use other benign furanic solvents such as, e.g. 2-ethylfuran, 2,5-dimethylfuran and 2,4-dimethylfuran for the preparation of future SLP systems where higher concentrations of the components are desired.

Surprisingly, the COSMO-RS derived activity coefficients did not correlate with the experimentally measured molar solute fractions for both single component systems. One possible reason for this might be that the activity coefficients were computed at infinite dilutions, which was certainly not the case in the experiments. Furthermore, even when taking THF and DCM into account, the computed activity coefficients varied only by a \log_{10} factor of 0.8 and 1.8 for bpp and sebacate, respectively. Recently, COSMO-RS predicted solubilities of 10 active pharmaceutical ingredients in 25 different solvents were reported to deviate from the experimental values by a \log_{10} factor of 0.8 [62]. This clearly emphasizes that while COSMO-RS can be used to efficiently rank a high number of solvents, experimental evaluation of solubilities remains indispensable at present.

The promising experimental solubilities in MTBE, which was probably falsely removed by the CEASAR models, prompted us to re-evaluate other solvents rejected solely on the same ground. These solvents were restricted to those that have better predicted solubilizing power than MTBE according to Eq. (1) and are listed in SI Table S3. 8 additional solvent candidates were identified with, 4 containing ether groups

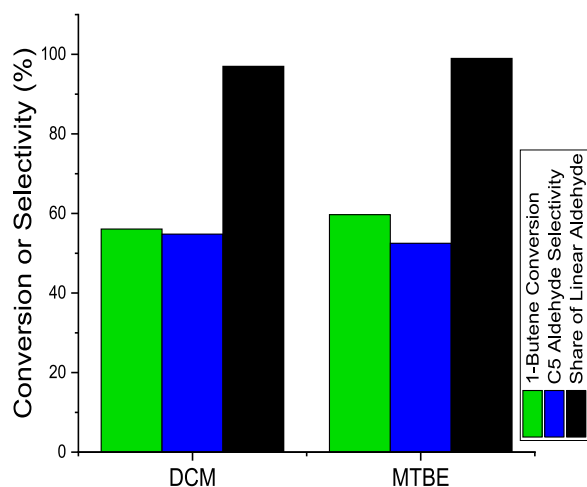


Fig. 4. Catalytic performance of monolithic SLP Rh-bpp-sebacate system (Rh:bp:sebacate = 1:4:16) prepared with DCM and MTBE, respectively, in 1-butene HyFo after 50 h TOS. Reaction conditions: 110 °C, 10 bar(a), flow rates of CO, H₂, 1-butene, and N₂ as reported in Table S1. MTBE: methyl *tert*-butyl ether, DCM: dichloromethane.

and 4 alkene and alkyne groups. The PARIS III solvent replacement tool does not provide the very relevant “inhalation impact” factor for any of these solvents, which might indicate that they are not widely used/accessible and that their real hazard potential has not yet been thoroughly studied.

3.3. Catalytic performance of SLP catalysts

Since MTBE was able to dissolve both bpp and sebacate at sufficiently high concentrations to meet the design range for the SLP catalyst preparation, and its usage in demonstration plant would not necessitate further regulatory work (*vide supra*), a monolithic Rh-bpp-sebacate SLP system was prepared with MTBE and benchmarked for 1-butene HyFo against an analogous SLP system prepared with DCM. Fig. 4 shows the catalytic performance of the two SLP catalysts after 50 h TOS and SI Fig. S5 shows the time resolved data.

The two SLP catalysts performed essentially equally well both in terms of catalytic activity, as indicated by the 1-butene conversion (58–60%), and the total selectivity towards aldehyde products (57–59%) (differences were within the limits of reproducibility of this type of performance measurements [63]). The very dynamic nature of the 1-butene conversion of the DCM-based catalyst during the initial 22 h start-up phase (Fig. S5) is in line with previous observations [63], and its cause is subject of a future study. Important for industrial application, the linear aldehyde selectivity (*n*-pentanal) was also very high (>98%) for both systems, corroborating that the bpp ligand was not degraded during catalyst preparation by, e.g. hydrolysis or oxidation. In combination, this indicates that alteration of the impregnation solvent from DCM to MTBE did not change the amount or distribution of catalytically active Rh-bpp complexes in the catalysts, which might have been the case if different solvation effects or other factors had led to permanent segregation of bpp and sebacate or a very unfavourable distribution of the liquid phase under operating conditions.

4. Conclusions

The present study demonstrates both the versatility and limitations of *in-silico* aided solvent screening tools. While COSMO-RS has helped to widen the scope of DCM replacement candidates in the preparation of monolithic SLP HyFo catalysts from the commonly quoted ethers and esters to include alkenes and alkynes, lack of correlation between

computed activity coefficients and experimentally determined solubilities of bpp and sebacate in five solvents with strong solubilizing power has established that experimental work is indispensable. QSAR-based predictions of mutagenicity and carcinogenicity led to the exclusion of a common DCM replacement (MTBE) on false grounds. Experimental solubility evaluation of four potential ether or ester solvent replacements suggested that bpp solubility was influenced by the presence of sebacate in the solvent. Hence, in MTBE the addition of sebacate clearly increased the solubility of bpp ligand, while the ligand only slightly lowered the solubility of sebacate. The effect of substituting DCM with MTBE in the preparation of the monolithic SLP catalysts was confirmed to be negligible on the catalytic performance of the catalysts for 1-butene HyFo, which in perspective makes the SLP catalysts more viable for industrial implementation with respect to EHS and regulatory aspects. Future proofing against potential needs for higher solute concentration was accomplished in the form of THF, which might imply that less hazardous furanes, such as 2-ethylfuran and 2,5-dimethylfuran, currently not tested due to their high boiling points, might be additional options. Two relatively benign solvents (MP and DMM) exhibited solubilities corresponding to the mid design range and might become relevant in case of tightened MTBE regulation.

CRedit authorship contribution statement

Leonhard Schill: Writing – original draft, Visualization, Methodology, Investigation. **Mahtab Madani:** Writing – original draft, Visualization, Investigation. **Bernd Hannebauer:** Writing – review & editing, Software, Investigation. **Robert Franke:** Writing – review & editing, Resources, Funding acquisition. **Rasmus Fehrmann:** Writing – review & editing, Supervision. **Anders Riisager:** Writing – review & editing, Writing – original draft, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors have no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.grets.2024.100102>.

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