Measuring and Predicting the Extraction Behavior of Biogenic Formic Acid in Biphasic Aqueous/Organic Reaction Mixtures

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ABSTRACT: The distribution coefficients and selectivities required for extraction purposes were predicted with a thermodynamic equation of state for the ternary system formic acid/water/extraction solvent. These predictions were validated with experimental data from the literature and experimental data from the oxidation of biomass to formic acid process measured in this work. Extraction solvents discussed in this work are 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-decanol, ethyl n-butyl ether, diisopropyl ether, di-n-butyl ether, benzyl formate, and heptyl formate. The considered temperature ranged from 273 to 363 K under atmospheric pressure. Perturbed-chain statistical associating fluid theory (PC-SAFT) was used for prediction purposes applying an approach as simple as possible and as complex as necessary to achieve trustworthy data for selecting the best extraction solvent. Using PC-SAFT allowed identifying 1-hexanol as the most promising solvent out of the 11 extraction agents. The predicted data were in good agreement with the experimental distribution coefficients and the selectivities, which are very sensitive to experimental uncertainties.

1. INTRODUCTION

The significance of replacing fossil-based energy systems with renewables has increased considerably in the last few years. The upcoming requirements for sustainable production of chemicals will lead to an increasing substitution of fossil fuels by biorenewable feedstock. This fact makes the research for alternative renewable energy sources more and more essential.¹ In this context, the group of Wasserscheid and Albert presented a catalytic reaction system that converts biomass selectively into formic acid (FA), which is called the “OxFA process”.²⁻⁵ This exothermic selective biomass oxidation process operates under mild conditions below 373 K at typically 20–30 bar oxygen pressure in homogeneous media. As water is used as green and benign solvent in combination with molecular oxygen or synthetic air as oxidizing agent, this process is highly sustainable. Moreover, biomass of different origin, composition, and humidity can be applied without necessary pretreatment. Furthermore, FA is produced as the only product in liquid phase at full conversion and therefore tedious separation processes can be avoided.⁶⁻⁵ The only side product is pure CO₂ that is formed in the gas phase and can be reused for the production of new biomass substrate, i.e., algae. The isolated product FA can be used in a broad range of applications such as platform chemical for transfer hydrogenations, silage preservation agent in the agricultural industry, additive for rubber applications, or drilling fluid in fracking.⁶ Moreover, FA is intensively discussed as a suitable storage compound for renewable hydrogen as it is liquid, only mildly toxic, and easy to handle under ambient conditions. The unique nature of FA allows either easy and selective decomposition to hydrogen and carbon dioxide (CO₂) through metal-catalyzed processes under very mild conditions⁷ or thermally induced decomposition to carbon monoxide and water at higher temperatures.⁵

The selective catalytic oxidation of biomass to FA is predominantly dependent on the selection of the right catalyst. In the previous studies, Keggin-type polyoxometalates (POMs) of the series [H₃₋₅PVₓMo₁₂₋₄₋₅O₄₀] (also known as HPA-n) have been reported to be appropriate for the reaction under consideration.⁶⁻⁹ Briefly, polyoxometalates (POMs) are well-defined metal oxoanions linked with oxygen bridges of early transition metals, and they can also contain heteroatoms to improve their chemical and thermal stabilities.¹⁰ POMs are especially resistant against hydrolytic and oxidative degradations.¹¹

Astonishingly, Albert et al. could demonstrate that in situ extraction of the formed FA from the aqueous reaction mixture using long-chain primary alcohols has a very positive effect on the overall FA yield.¹² This very surprising effect can be explained by a pH drop during the FA formation in the aqueous reaction phase that lowers the catalyst selectivity. This negative influence can be overcome by using a biphasic reaction system, where the pH level of the aqueous reaction phase is kept constant as the formed FA is partially extracted into the organic alcohol phase. So far, both catalytic activity and an improved selectivity of the POM-catalyzed reaction system can be realized using this approach. Using this straightforward in situ extraction system with 1-
hexanol as the best-performing extracting agent, maximum FA yields of 85% from glucose and 61% from water-insoluble beech could be realized.12

Besides a suitable catalyst, finding the best extraction solvent is a time-consuming task. For that purpose, usually experiments are designed, which are chosen by experienced engineers. However, the amount of possible extraction solvents is very large and thus methods have been developed toward an easier, faster, and less expensive way of rating extraction solvents. Among such methods, Hansen solubility parameters,13 Robbins chart of solute—solvent interaction14 for qualitative indication, modified separation of cohesive energy density,15 or thermodynamic models can be found.16 The latter are able to correlate or predict liquid—liquid phase equilibria (LLE), which finally allow calculating distribution coefficients and selectivity. On the basis of these properties, the thermodynamically optimal extraction solvent can be found. In recent years, the LLE of the ternary system FA/water/extraction solvent has been investigated experimentally and correlated with various thermodynamic models. Senol17 measured the LLE of FA/water/1-octanol and experimentally and correlated with various thermodynamic properties, the thermodynamically optimal extraction selectivities of biogenic FA from the OxFA process between aqueous reaction media and organic extraction phase. Additionally, the influence of the homogeneous HPA-5 (H₃PV₅MoO₁₄) catalyst (present in the aqueous phase) on the experimental distribution coefficients and extraction selectivities was investigated with data stemming from real reaction mixtures at 363 K and validated with PC-SAFT.

2. METHODS

2.1. Distribution Coefficients and Selectivities. On the basis of experimental LLE data of ternary mixtures, the sensitive properties distribution coefficient $D^{ex}_{FA}$ and selectivity $S^{ex}_{FA,H₂O}$ were calculated

$$D^{ex}_{FA} = \frac{c^{ex}_{FA}}{c^{aq}_{FA}}$$

(1)

$$S^{ex}_{FA,H₂O} = \frac{D^{ex}_{FA}}{D^{ex}_{H₂O}}$$

(2)

where $c^{ex}_{FA}$ is the molar concentration of formic acid in the extraction solvent-rich or the water-rich phase. The distribution coefficient for water $D^{ex}_{H₂O}$ was calculated as follows

$$D^{ex}_{H₂O} = \frac{c^{aq}_{H₂O}}{c^{aq}_{H₂O}}$$

(3)

where $c^{aq}_{H₂O}$ is the molar concentration of water in the extraction solvent-rich phase (“aq”) or the water-rich phase (“aq”).

The intention is to select an extraction solvent with a high miscibility of FA and a low solubility of water. Consequently, high $D^{ex}_{FA}$ values and high $S^{ex}_{FA,H₂O}$ values are desired for optimal separation.

2.2. Thermodynamic Modeling Using PC-SAFT. To model phase equilibrium such as LLE using PC-SAFT, the residual Helmholtz energy, $a^{res}$, which serves as a basis for all calculations, is used.

$$a^{res} = a^{hc} + a^{disp} + a^{assoc}$$

(4)

The residual Helmholtz energy in eq 4 is expressed as the sum of different Helmholtz-energy contributions caused by hard-chain repulsion $a^{hc}$, dispersion $a^{disp}$, and hydrogen bonding $a^{assoc}$. For further information, the reader is referred to the original publications by Gross and Sadowski.21,22 Multipolar and ionic effects were not considered in this work. Water, FA, and alcohols were modeled as associating fluids according to the 2B association scheme with two association sites, which are one proton donor and one proton acceptor, each. To characterize a self-associating component, five pure-component parameters are required: segment diameter $\sigma$, segment number $m^{res}$, dispersion-energy parameter $u/k_B$, association-energy parameter $\gamma^{assoc}/k_B$.

$$a^{hc} = 4\pi n \sigma^2$$

$$a^{disp} = \frac{3}{2} \pi n \sigma^2$$

$$a^{assoc} = \frac{1}{2} \pi n \sigma^2$$

In this work, PC-SAFT was used to predict the distribution coefficients and selectivities of biogenic FA from the oxidation of biomass to formic acid (OxFa) process between aqueous reaction media and organic extraction solvent for one of the following extraction solvents: di-n-butyl ether, diisopropyl ether, ethyl n-butyl ether, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-decanol, benzyl formate, and heptyl formate, according to Reichert et al.12 All investigations were performed under atmospheric pressure. The PC-SAFT predictions were validated with experimental data from the literature and from this work. The focus was keeping the amount of experimental input data to a minimum extent while still generating accurate predictions. The work first compares PC-SAFT predictions with experimental results of artificial model systems16,20 under isothermal conditions, prior to evaluating the temperature influence on the system at different temperatures. Finally, PC-SAFT was applied to predict distribution coefficients and extraction selectivities of biogenic FA from the OxFA process between aqueous reaction media and organic extraction phase.
and association-volume parameter $\kappa_{AB}$. Components that do not interact via self-association are characterized with three pure-component parameters $\sigma_i$, $m_i^{eq}$, and $u_i/k_i$.

The segment diameter and the dispersion-energy parameter of a mixture were calculated by applying the conventional combining rules of Lorentz and Berthelot.

$$\sigma_i = \frac{1}{2}(\sigma_i + \sigma_j)$$  \hspace{1cm} (5)

$$u_i = \sqrt{u_i u_j (1 - k_i)}$$  \hspace{1cm} (6)

In eq 6, $k_i$ is the binary interaction parameter, which might be used to correct deviations of the mixture parameters from the means of the pure-component parameters. The cross-association parameters $\epsilon_{AB}$ and $\kappa_{AB}$ were calculated using the formalism by Wolbach and Sandler.

$$\epsilon_{AB} = \frac{1}{2}(\epsilon_{A} + \epsilon_{B})$$  \hspace{1cm} (7)

$$\kappa_{AB} = \sqrt{\kappa_{A} \kappa_{B} \kappa_{AB}} \left[ \frac{1}{2}(\sigma_i + \sigma_j) \right]^{3}$$  \hspace{1cm} (8)

All interaction parameters used in this work are only valid with the corresponding pure-component parameters listed in Table 1.

### 2.2.1. Liquid–Liquid Equilibria

The LLE of multicomponent systems was modeled on the basis of solving the isofugacity criterion between the two liquid phases according to

$$x_i \varphi_i = x_j \varphi_j$$  \hspace{1cm} (9)

with the mole fraction $x_i$ and the fugacity coefficient $\varphi_i$ of component $i$. PC-SAFT was applied to predict fugacity coefficients in mixtures, which depend on the kind of components, mixture composition, density, and temperature. To calculate the molar fractions of the two coexisting phases at equilibrium, eq 9 was solved iteratively, which required good starting values. To generate good starting values, the Gibbs free-energy difference $\Delta g$ was minimized. The stability criterion of a heterogeneous system can be formulated as

$$\Delta g(T, p, x_i) = g - \sum_{l=1}^{\infty} a^{l} \varphi_{l}^{l}$$  \hspace{1cm} (10)

Table 1. PC-SAFT Pure-Component Parameters for Formic Acid, Water, and the Extraction Solvents Studied in This Work

| compound                  | $m_i^{eq}$ | $\sigma_i$ (Å) | $u_i/k_i$ (K) | $\epsilon_{AB}/k_i$ (K) | $\kappa_{AB}$ | ref   |
|---------------------------|------------|----------------|---------------|--------------------------|--------------|-------|
| water                     | 1.2047     |                | 353.95        | 2425.7                   | 0.0451       | 35    |
| formic acid               | 1.2956     | 3.3396         | 186.94        | 2670.5                   | 0.298384     | 36    |
| di-n-butyl ether          | 4.4334     | 3.6959         | 228.48        |                          | 37    |
| diisopropyl ether         | 3.6987     | 3.6311         | 212.04        |                          | 38    |
| ethyl n-butyl ether       | 3.5966     | 3.6599         | 232.04        |                          | 38    |
| 1-butanol                 | 2.7515     | 3.6139         | 259.59        | 2544.6                   | 0.006692     | 31    |
| 1-pentanol                | 3.6260     | 3.4508         | 247.28        | 2252.1                   | 0.010319     | 31    |
| 1-hexanol                 | 3.5146     | 3.6735         | 262.32        | 2538.9                   | 0.005747     | 31    |
| 1-heptanol                | 4.3985     | 3.5450         | 253.46        | 2878.5                   | 0.001155     | 31    |
| 1-oktanol                 | 4.3555     | 3.7145         | 262.74        | 2754.8                   | 0.002197     | 31    |
| 1-decanol                 | 4.7658     | 3.8465         | 267.30        | 2776.4                   | 0.003445     | 39    |
| benzyl formate            | 3.3955     | 3.7349         | 325.16        |                          |              |
| heptyl formate            | 4.5705     | 3.6484         | 253.32        |                          |              |

In eq 10, $g$ describes the Gibbs free energy of the system, if it stays homogeneous; the sum identifies the Gibbs free energy if the system separates into more than one phase. Thus, if $\Delta g$ in eq 10 becomes negative, the system splits into two phases, where $\varphi_{xx}$ describes the molar phase fraction of phase $x$ and $\varphi$ denotes the number of phases present.

#### 2.2.2. Distribution Coefficients and Selectivities

PC-SAFT was used to predict the mole fraction of each component in the two liquid phases, which were then converted to distribution coefficients $D_{FA}^{PC-SAFT}$ and $D_{H_{2}O}^{PC-SAFT}$ with

$$D_{FA}^{PC-SAFT} = \frac{x_{FA}^{extr} \varphi_{H_{2}O}^{extr}}{x_{FA}^{extr} \varphi_{FA}^{extr}}$$  \hspace{1cm} (11)

$$D_{H_{2}O}^{PC-SAFT} = \frac{x_{H_{2}O}^{extr} \varphi_{FA}^{extr}}{x_{H_{2}O}^{extr} \varphi_{H_{2}O}^{extr}}$$  \hspace{1cm} (12)

where $x_i$ is the molar fraction of component $i$ in the extraction solvent-rich phase or the water-rich phase and $\rho$ is the density of the equilibrium phase, which was predicted using PC-SAFT in this work. This is a valid method as the accuracy of the density predictions of liquid equilibrium phases was confirmed by Reschke et al. for complex systems. The molar mass $M$ of the phases was calculated by eq 13 using the molar fraction $x_i$ and the molar mass $M_i$ of each component.

$$\bar{M} = \sum_{i} x_i M_i$$  \hspace{1cm} (13)

The predicted selectivity $S_{FA,H_{2}O}^{PC-SAFT}$ is defined in analogy to eq 2.

#### 3. RESULTS AND DISCUSSION

##### 3.1. PC-SAFT Results

PC-SAFT was used to model the LLEs of all binary and ternary systems considered in this work to predict $D_{FA}$ and $S_{FA,H_{2}O}$. Prior to predicting the latter, PC-SAFT parameters were required. All pure-component parameters and their references are listed in Table 1. Prior to predicting LLE in ternary systems FA/water/extraction solvent, the LLE between water and each of the extraction solvents was modeled with PC-SAFT. For this purpose, $k_i$ values were fitted to experimental LLE data of binary systems water/extraction solvent. The deviations between PC-SAFT-predicted LLE and experimental data were minimized. The stability criterion of a heterogeneous system can be formulated as

$$\Delta g(T, p, x_i) = g - \sum_{l=1}^{\infty} a^{l} \varphi_{l}^{l}$$  \hspace{1cm} (10)
LLE data were minimized and evaluated in terms of the average relative deviation (ARD), which was calculated as

$$\text{ARD} = 100 \times \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \left| 1 - \frac{w_{i}^{\text{PC-SAFT}}}{w_{i}^{\text{exp}}} \right|$$

(14)

where NP is the number of data points and \(w_{i}\) is the mass fraction of a component \(i\). To accurately model temperature-dependent LLE, the binary interaction parameter \(k_{ij}\) was assumed to depend linearly on temperature

$$k_{ij} = k_{ij}^{\text{ref}} + k_{ij,T}(T - T^{\text{ref}})$$

(15)

The results for the \(k_{ij}\) values obtained by minimizing the ARD in eq 14 using the experimental data with minimizing the ARD in Table 2.

Having the pure-component and binary PC-SAFT parameters at hand, \(D_{\text{FA}}^\text{PC-SAFT}\) and \(S_{\text{FA,H}_2\text{O}}^\text{PC-SAFT}\) values were predicted. In the following, the prediction results are divided into artificial modeling systems FA/water/extraction solvent at 298 K (Section 3.1.1), at temperatures up to 363 K that also might contain catalyst (Section 3.1.2), as well as for the real reaction mixture containing catalyst (Section 3.1.3).

3.1.1. \(D_{\text{FA}}\) and \(S_{\text{FA,H}_2\text{O}}\) of the Artificial Model System at 298 K.

In a first step of this work, the LLE of the ternary model system FA/water/1-decanol was predicted with PC-SAFT at 298 K under atmospheric pressure. In this artificial system, catalyst was not present during the experimental measurements. Experimental data were available from the literature for FA/water/1-decanol, as well as for X = 1-decanol by Gilani and Asan.\(^{16}\) It was found that the LLE of these mixtures were modeled accurately by fitting one binary \(k_{ij}\) between FA and water to data of the ternary system FA/water/1-decanol, which thus presents the reference correlation system. The slope of the tie lines as well as the equilibrium weight fractions in the nonaqueous phase was modeled accurately using this approach. The same \(k_{ij}\) between FA and water was used to predict LLE of all other ternary systems FA/water/alcohol. For the system FA/water/1-decanol, an additional immiscibility between FA and 1-decanol was found from experimental data, which required adjusting one \(k_{ij}\) between FA and 1-decanol to LLE data of the binary mixture FA/1-decanol. All of these \(k_{ij}\) values are given in Table 2. Figure 1 shows the comparison of \(D_{\text{exp}}^\text{FA}\) with \(D_{\text{FA}}^\text{PC-SAFT}\). It can be seen that for 1-butanol \(D_{\text{FA}}^\text{PC-SAFT}\) is correlated well with \(D_{\text{FA}}^\text{PC-SAFT}\) and the predicted values of \(D_{\text{FA}}^\text{PC-SAFT}\) for the other alcohols are in excellent agreement with the experimental values. For increasing C-chain length of the alcohols, the \(D_{\text{FA}}^\exp\) values are decreasing, which is caused by the decreasing slope of the tie line from water to the extraction solvent. The decrease of \(D\) values with increasing C-chain length has been already observed in the extraction of acetic acid with 1-alkanols.\(^{59}\) Further, \(D\) values of 1-butanol were found to be much higher than those of 1-pentanol (and of 1-propanol) in the extraction of paracetamol from aqueous solution under salting-out conditions.\(^{50}\)

The ternary LLE including tie lines can be accurately predicted by PC-SAFT. Figure 2 compares \(S_{\text{FA,H}_2\text{O}}^\text{PC-SAFT}\) and \(S_{\text{FA,H}_2\text{O}}^{\exp}\) for various alcohols. It can be observed from Figures 1 and 2 that the system with 1-decanol differs significantly from the systems containing other 1-alcohols under investigation. The selectivity and distribution coefficients become comparatively small values. This unexpected experimental behavior can be predicted with PC-SAFT accurately in the mixture with 1-decanol. The reason behind such experimental behavior is the fact that among all alcohols studied, only 1-decanol partially demixes with FA; however, this is accurately described by PC-SAFT as well.

3.1.2. \(D_{\text{FA}}\) and \(S_{\text{FA,H}_2\text{O}}\) of Artificial Model System between 298 and 363 K.

In a next step, the temperature dependency of
comparisons $D_{\text{exp}}^\text{PC-SAFT}$ and $D_{\text{exp}}^\text{PP}$ for the extraction solvents: 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol. The absence of 1-butanol is due to the fact that FA/water/1-butanol is a homogeneous mixture at 363 K. It can be observed that $D_{\text{exp}}^\text{PP}$ decreases over the length of the C-chain, which is also predicted accurately with PC-SAFT. This means that accurate predictions are possible with PC-SAFT that do not require binary parameters except as those between water and extraction solvent. Consequently, for all systems, the $k_{ij}$ values between water and FA were set to zero at 363 K.

To account for temperature dependency, $k_{ij}$ between FA and water was assumed to decrease linearly with decreasing temperature according to eq 15. This allowed a reasonably good agreement between $D_{\text{exp}}^\text{PC-SAFT}$ and $D_{\text{exp}}^\text{PP}$. Similarly, also the $k_{ij}$ value for FA/1-decanol was found to be equal to zero at 363 K and to decrease linearly with increasing temperature. Hence, the $D_{\text{exp}}^\text{PC-SAFT}$ at 363 K is predicted with only the temperature-dependent $k_{ij}$ between water and the extraction solvents, whereas the prediction model is kept as simple as possible. Figure 4 illustrates $D_{\text{exp}}^\text{PC-SAFT}$ and $D_{\text{exp}}^\text{PP}$ and their dependence on temperature considering various extraction alcohols. At temperatures above 298 K, the mixture FA/water/1-butanol is homogeneous and LLE was not found with PC-SAFT as well (no $D_{\text{exp}}^\text{PC-SAFT}$ values above 298 K). The increase of $D_{\text{exp}}^\text{PP}$ with temperature is predicted also with PC-SAFT.

### 3.1.3. Predicting the Extraction Using Data from OxFA Process

In a final step within this work, $D_{\text{exp}}$ and $S_{\text{FA,H2O}}$ were predicted with PC-SAFT at 363 K under atmospheric pressure for real systems. That means these data originated from the OxFA process, where the homogeneous HPA-5 catalyst converts several biogenic substrates to FA in aqueous phase. The produced biogenic FA is removed in situ from the reaction mixture using suitable organic extracting agents. These data are available in Reichert et al.15 The data measured consequently stem from mixtures that contain biogenic FA, water, extracting agent, possible side products or nonconverted substrates, and the HPA-5 catalyst. In this work, $D_{\text{exp}}$ and $S_{\text{FA,H2O}}$ values stemming from these complex real systems were predicted with PC-SAFT assuming only FA, water, and extraction solvents present in the mixtures. The predictions were based on the pure-component parameters and on one binary parameter between water and the extraction solvent, as presented in Tables 1 and 2. This rough modeling approach nevertheless might yield a good estimation to select the most thermodynamically promising solvent for FA extraction from aqueous reaction media.

In Figure 5, the comparison of $D_{\text{exp}}^\text{PC-SAFT}$ and $D_{\text{exp}}^\text{PP}$ is illustrated, and in Figure 6, $S_{\text{FA,H2O}}^\text{PC-SAFT}$ and $S_{\text{FA,H2O}}^\text{PP}$ are compared for various conditions.
work PC-SAFT is used to get a very good estimation of the potentials of extraction solvents. The aim is not to have the most accurate prediction, which implies introducing more binary interaction parameters and fitting them to experimental data, but to have at least a method in hand that is able to reliably predict the qualitative behavior of different extraction solvents and thus can be used as a solvent-screening tool for FA extraction from aqueous reaction mixtures.

4. CONCLUSIONS

In this work, distribution coefficients and selectivities of the system FA/water with different extraction solvents were predicted with PC-SAFT and compared to measured data from this work and from the literature. The investigated extraction solvents were 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-decanol, ethyl n-butyl ether, diisopropyl ether, di-n-butyl ether, benzyl formate, and heptyl formate. The predictions were compared to the data of artificial model systems at 298.15 K (system without catalyst and side products), data of systems under temperature conditions near real reaction conditions (up to 363.15 K), and data of systems from real reaction broth at 363.15 K. All data were determined under atmospheric pressure. The PC-SAFT model was used to predict the ternary systems without any knowledge of the latter and with a minimum amount of data required for binary subsystems. For all predictions, the pure-component PC-SAFT parameters and the binary interaction parameters between water and the extraction solvent were required. It was found that these \( k_{ij} \) parameters were required between components, which form a miscibility gap. Applying this approach allowed predicting the LLE and the derived properties distribution coefficient and selectivity, which are very sensitive properties. This highlights the advantage of using physical-based models over correlations as it means a significant reduction of required experimental data and further explains the occurrence of unexpected behavior of distribution coefficient and selectivity with respect to the chain length of the extraction solvent.

5. EXPERIMENTAL SECTION

5.1. Experimental Determination of Extraction Parameters. All chemicals were obtained commercially and used without further purification. The HPA-5 catalyst \( \text{H}_4[\text{PV}_{5}\text{Mo}_{7}\text{O}_{40}]\cdot12\text{H}_2\text{O} \) was synthesized according to the literature.\(^4\),\(^34\) The characterization via inductively coupled plasma optical emission spectrometry (ICP-OES) resulted in a P/V/Mo ratio of 1.4/93/7.05. ICP-OES measurements were conducted on a PerkinElmer Plasma 400 instrument, and NMR spectra were recorded on a Jeol ECX-400 MHz spectrometer. Gaseous sample analyses were performed using a Varian GC 450 equipped with a 2 m × 0.75 mm ID ShinCarbon ST column.

5.2. Catalytic Oxidation Reactions (Monophasic OxFA Process). The oxidation reactions were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. Water (100 g), 0.5 mmol (0.91 g) HPA-S, and 10 mmol (1.80 g) glucose were charged into the vessel. The system was purged three times with oxygen, the stirrer was set to 300 rpm, and heating was started. When the desired temperature of 363 K was reached, the oxygen pressure was increased to 20 bar and the stirrer was set to 1000 rpm.

5.3. Ex Situ Extraction. After oxidizing a solution containing 1.80 g of glucose, 0.91 g of HPA-S, and 100.0 g of \( \text{H}_2\text{O} \) for 6 h at 363 K under 20 bar oxygen pressure, FA formation was determined by \(^1\text{H}\) NMR spectroscopy. The extraction solvent was stirred for 2 h at 1000 rpm.
(100.0 g) was preheated to 363 K and then added to the reaction mixture, resulting in a liquid–liquid biphasic mixture that was stirred for 1 h at 363 K under ambient pressure. The biphasic solution was separated, and a sample of each phase was taken and analyzed by means of $^1$H NMR spectroscopy to determine the FA content.

5.4. Oxidation Experiments with in Situ Extraction (Biphasic OxFa Process). For the oxidation experiments with in situ extraction, substrate (1.80 g glucose), 0.91 g of HPA-5 was charged into the reactor. The system was purged three times with oxygen and then the reactor was heated to the reaction temperature with stirring at 300 rpm. When reaching 363 K, oxygen pressure and stirrer speed were set to the desired values. After the experiments, both liquid phases were analyzed by $^1$H NMR spectroscopy to determine their FA content.

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Notes
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■ REFERENCES
(1) Shafiee, S.; Topal, E. When will fossil fuel reserves be diminished? Energy Policy 2009, 37, 181–189.
(2) Albert, J.; Wölfel, R.; Bößmann, A.; Wasserscheid, P. Selective oxidation of complex, water-insoluble biomass to formic acid using additives as reaction accelerators. Energy Environ. Sci. 2012, 5, 7956–7962.
(3) Albert, J.; Wasserscheid, P. Expanding the scope of biogenic substrates for the selective production of formic acid from water-insoluble and wet waste biomass. Green Chem. 2015, 17, 5164–5171.
(4) Albert, J.; Lüders, D.; Bößmann, A.; Guldi, D. M.; Wasserscheid, P. Spectroscopic and electrochemical characterization of heteropoly acids for their optimized application in selective biomass oxidation to formic acid. Green Chem. 2014, 16, 226–237.
(5) Albert, J.; Mehler, J.; Tucher, J.; Kastner, K.; Streb, C. One-step synthesizable Lindqvist-isopolyoxometalates as promising new catalysts for the selective conversion of glucose as a model substrate for lignocellulosic biomass to formic acid. ChemistrySelect 2016, 1, 2889–2894.
(6) Reutemann, W.; Kieczea, H. Ullmann’s Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005.
(7) Albert, J.; Jess, A.; Kern, C.; Pöllymann, F.; Glowienka, K.; Wasserscheid, P. Formic acid-based Fischer-Tropsch synthesis for green fuel production from waste wheat biomass and renewable excess energy. ACS Sustainable Chem. Eng. 2016, 4, 5078–5086.
(8) (a) Bodden, A.; Loges, B.; Junge, H.; Beller, M. Hydrogen generation at ambient conditions: application in fuel cells. ChemSusChem 2008, 1, 751–758. (b) Enthaler, S.; von Langermann, J.; Schmidt, T. Carbon dioxide and formic acid-the couple for environmental-friendly hydrogen storage? Energy Environ. Sci. 2010, 3, 1207–1217. (c) Sutton, A. D.; Waldie, F. D.; Wu, R.; Schlaf, M.; Silks, L. A. P.; III; Gordon, J. C. The hydrodeoxygenation of bioderived furans into alkanes. Nat. Chem. 2013, 5, 428.
(9) (a) Albert, J. Selective oxidation of lignocellulosic biomass to formic acid and high-grade cellulose using tailor-made polyoxometalate catalysts. Faraday Discuss. 2017, 202, 99–109. (b) Albert, J.; Preuster, P. Biogenic formic acid as a green hydrogen carrier. Energy Technol. 2017, DOI: 10.1002/ente.201700572.
(10) (a) Hill, C. L.; Prosser-McCarthy, C. M. Homogeneous catalysis by transition metal oxygen anion clusters. Coord. Chem. Rev. 1995, 143, 407–455. (b) Lechner, M.; Gütel, R.; Streb, C. Challenges in polyoxometalate-mediated aerobic oxidation catalysis: catalyst development meets reactor design. Dalton Trans. 2016, 45, 16716–16726.
(11) (a) Amman, M. Polyoxometalates: formation, structures, principal properties, main deposition methods and application in sensing. J. Mater. Chem. A 2013, 1, 6291–6312. (b) Miras, H. Y.; Yan, J.; Long, D. L.; Cronin, L. Engineering polyoxometalates with emergent properties. Chem. Soc. Rev. 2012, 41, 7403–7430.
(12) Reichert, J.; Brunner, B.; Jess, A.; Wasserscheid, P.; Albert, J. Biomass oxidation to formic acid in aqueous media using polyoxometalate-catalysts boosting FA selectivity by in-situ extraction. Energy Environ. Sci. 2015, 8, 2985–2990.
(13) Hansen, C. M. Hansen Solubility Parameters: A User’s Handbook; CRC press, 2007.
(14) Robbins, L. Liquid-liquid extraction: A pretreatment process for wastewater. Chem. Eng. Prog. 1980, 76, 58–61.
(15) Thomas, E. R.; Eckert, C. A. Prediction of limiting activity coefficients by a modified separation of cohesive energy density model and UNIFAC. Ind. Eng. Chem. Process Des. Dev. 1984, 23, 194–209.
(16) Gilani, H. G.; Asan, S. Liquid-liquid equilibrium data for systems containing of formic acid, water, and primary normal alcohols at T = 298.2 K. Fluid Phase Equilib. 2013, 354, 24–28.
(17) Senol, A. Liquid-liquid equilibria for ternary systems of (water+carboxylic acid+1-octanol) at 293.15 K: modeling phase equilibria using a solvatochromatic approach. Fluid Phase Equilib. 2005, 227, 87–96.
(18) Özmen, D. Determination and correlation of liquid-liquid equilibria for the (water+carboxylic acid+dimethyl maleate) ternary systems at T = 298.2 K. Fluid Phase Equilib. 2008, 269, 12–18.
(19) Bilgin, M.; Birman, I. Liquid phase equilibria of (water+formic acid+diethyl carbonate or diethyl malonate or diethyl fumarate) ternary systems at 298.15 K and atmospheric pressure. Fluid Phase Equilib. 2011, 302, 249–253.
(20) Gilani, H. G.; Azadian, M. Tie-line data for water-formic acid-1-decanol ternary system at T = 298.2, 303.2, 313.2, and 323.2 K. Thermochim. Acta 2012, 547, 141–145.
(21) Eckert, F.; Klant, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. AIChE J. 2002, 48, 369–385.
(22) Dufal, S.; Papaioannou, V.; Sadeqzadeh, M.; Pogiatzis, T.; Chemros, A.; Adjiman, C. S.; Jackson, G.; Galindo, A. Prediction of thermodynamic properties and phase behavior of fluids and mixtures with the SAFT-$\gamma$ Mic group-contribution equation of state. J. Chem. Eng. Data 2014, 59, 3272–3288.
(23) Nann, A.; Held, C.; Sadowski, G. Liquid-liquid equilibria of 1-butanol/water/IL systems. Ind. Eng. Chem. Res. 2013, 52, 18472–18481.
(24) Laubs, F.; Klein, T.; Sadowski, G. Partition coefficients of pharmaceuticals as functions of temperature and pH. Ind. Eng. Chem. Res. 2015, 54, 3968–3975.
(25) Riechert, O.; Zeiner, T.; Sadowski, G. Measurement and modeling of phase equilibria in systems of acetoniitrile, n-alkanes, and beta-myrice. Ind. Eng. Chem. Res. 2015, 54, 1153–1160.
(26) Mohammad, S.; Grundl, G.; Müller, R.; Kunz, W.; Sadowski, G.; Held, C. Influence of electrolytes on liquid-liquid equilibria of water/1-butanol and on the partitioning of S-hydroxymethylfurfural in water/1-butanol. Fluid Phase Equilib. 2016, 428, 102–111.
(27) Rodríguez-Palmeiro, I.; Rodríguez, O.; Soto, A.; Held, C. Measurement and PC-SAFT modelling of three-phase behaviour. Phys. Chem. Chem. Phys. 2015, 17, 1800–10.
(28) Lindvig, T.; Michelsen, M. L.; Kontogeorgis, G. M. Liquid–liquid equilibria for binary and ternary polymer solutions with PC-SAFT. Ind. Eng. Chem. Res. 2004, 43, 1125–1132.
(29) Corazza, M. L.; Fouad, W. A.; Chapman, W. G. PC-SAFT predictions of VLE and LLE of systems related to biodiesel production. Fluid Phase Equilib. 2016, 416, 130−137.
(30) Domżańska, U.; Paduszyński, K.; Królkowski, M.; Wróblewska, A. Separation of 2-phenylethanol from water by liquid-liquid extraction with ionic liquids: New experimental data and modeling with modern thermodynamic tools. Ind. Eng. Chem. Res. 2016, 55, 5736−5747.
(31) Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to associating systems. Ind. Eng. Chem. Res. 2002, 41, 5510−5515.
(32) Gross, J.; Sadowski, G. Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. Ind. Eng. Chem. Res. 2001, 40, 1244−1260.
(33) Reschke, T.; Brandenbusch, C.; Sadowski, G. Modeling aqueous two-phase systems: I. Polyethylene glycol and inorganic salts as ATPS former. Fluid Phase Equilib. 2014, 368, 91−103.
(34) Zhizhina, E. G.; Odyakov, V. F. Alteration of the physicochemical properties of catalysts based on aqueous solutions of Mo-V-P heteropoly acids in redox processes. React. Kinet. Catal. Lett. 2008, 95, 301−312.
(35) Fuchs, D.; Fischer, J.; Tumakaka, F.; Sadowski, G. Solubility of amino acids: Influence of the pH value and the addition of alcoholic cosolvents on aqueous solubility. Ind. Eng. Chem. Res. 2006, 45, 6578−6584.
(36) Cafrens, J. Modellierung Thermodynamischer Eigenschaften Pharmazeutischer Substanzen in Lösungsmitteln und Lösungsmittelgemischen; Verl. Dr. Hut, 2013.
(37) Kleiner, M.; Sadowski, G. Modeling of polar systems using PCP-SAFT: An approach to account for induced-association interactions. J. Phys. Chem. C 2007, 111, 15544−15553.
(38) Antón, V.; Muñoz-Embíd, J.; Artal, M.; Lafuente, C. Experimental and modeled volumetric behavior of linear and branched ethers. Fluid Phase Equilib. 2016, 417, 7−18.
(39) Albers, K.; Heilig, M.; Sadowski, G. Reducing the amount of PCP-SAFT fitting parameters. 2. Associating components. Fluid Phase Equilib. 2012, 326, 31−44.
(40) Gmehling, J.; Krafczyk, J.; Ahlers, J.; Nebig, S.; Hunecker, I.; Eisel, M.; Fischer, D.; Krentscher, B.; Beyer, K. Pure Compound Data from DDB; Dortmund Data Bank, 1983.
(41) Hopfe, D. Thermophysical Data of Pure Substances. In Data Compilation of FIZ CHEMIE; Wiley: Germany, 1990; Vol. 1.
(42) Samarov, A. A.; Nazmutdinov, A. G.; Verevkin, S. P. Vapour pressures and enthalpies of vaporization of aliphatic esters. Fluid Phase Equilib. 2012, 334, 70−75.
(43) Stephenson, R. Mutual solubilities: water-ketones, water-ethers, and water-gasoline-alcohols. J. Chem. Eng. Data 1992, 37, 80−95.
(44) Stephenson, R.; Stuart, J. Mutual binary solubilities: water-ethers and water-alcohols and water-esters. J. Chem. Eng. Data 1986, 31, 56−70.
(45) Stephenson, R.; Stuart, J.; Tabak, M. Mutual solubility of water and aliphatic alcohols. J. Chem. Eng. Data 1984, 29, 287−290.
(46) Lorentz, H. A. Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase. Ann. Phys. 1881, 248, 127−136.
(47) Berthelot, D. Sur le mélange des gaz. C. R. Hebd. Seances Acad. Sci. 1898, 126, 1703−1855.
(48) Wobst, J. P.; Sandler, S. I. Using molecular orbital calculations to describe the phase behavior of cross-associating mixtures. Ind. Eng. Chem. Res. 1998, 37, 2917−2928.
(49) Mahramanlioğlu, M.; Tuncay, M. The distribution coefficients of acetic acid between water and solvent systems. J. Eng. Sci. 2001, 7, 415−419.
(50) Nikolić, G. M.; Živković, J. V.; Atanasković, D. S.; Nikolić, M. G. Synergic effects in the extraction of paracetamol from aqueous NaCl solution by the binary mixtures of diethyl ether and low molecular weight primary alcohols. Russ. J. Phys. Chem. A 2013, 87, 2191−2194.