

# The influence of solvents and impurities on the separation of biobased phenol and 2-octanone

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## Abstract

**BACKGROUND:** Phenol is used as a raw material in the polycarbonate industry and as the incentive for bio-based plastics and products is increasing, so is the interest in and demand for bio-based phenols. In renewable phenol production processes based on biomass, impurities derived from the biomass, including other oxygenate compounds, are expected in the phenol containing solution. Vapor–liquid equilibrium (VLE) of phenol and 2-Octanone was studied and impact of impurities thereon to gain insights applicable for similar systems in biorefineries for renewable phenol production.

**RESULTS:** For the binary mixture of phenol - 2-octanone azeotropic VLE behavior was found. The effects of ternary compounds on the molecular interactions between phenol and 2-octanone were studied using isothermal calorimetry (ITC) and molecular modelling (MM), and the impact on the VLE behavior was measured using an ebulliometer.

**CONCLUSION:** It was found that the relative volatility could be improved by adding solvents that are polar and/or contain hydrogen bond accepting groups. Ketones and ethers most strongly improved the relative volatility of the binary mixture 2-octanone – phenol. Addition of a linear alkane, a repelling component especially for 2-octanone, strongly improved the relative volatility as well. ITC and MM results, providing heat of mixing and the interaction energy of mixture components, improved fundamental understanding of the molecular interactions between phenol, 2-octanone and ternary compounds, and supported the VLE findings.

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## INTRODUCTION

Phenol is used as a raw material in the polycarbonate industry and as the incentive for bio-based plastics and products is increasing, so is the interest in and demand for bio-based phenols.<sup>1–3</sup> Bio-based phenol can be produced from biomass resources using various processes,<sup>4–8</sup> as well as from industrial waste streams.<sup>9,10</sup> For both situations process streams with low phenol concentrations are obtained, and these streams need to be purified and concentrated to generate sufficiently pure phenol which can be used as raw material for polycarbonate production. Liquid–liquid extraction, e.g. with cumene,<sup>11–13</sup> can be used to remove phenol from aqueous (waste) streams. During (further) product purification, regeneration and recycling of the solvent is essential to realize a viable purification process.<sup>14</sup> In renewable phenol production processes based on biomass, impurities derived from the biomass, including other oxygenate compounds, are expected in the phenol containing solution. These impurities should be taken into account in the development of the separation processes since their

presence may not only affect the reactions and separation processes in the production and further processing, but also the recovery processes.<sup>4,5</sup> Among other types of impurities, also ketones may be expected, including ketones with pure component boiling points close to the boiling point of phenol.

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For example, 2-octanone and other ketones have been applied in liquid–liquid extraction of phenol from aqueous streams.<sup>15,16</sup>

In this work, vapor–liquid equilibria (VLE) for mixtures containing phenol and 2-octanone are described, and effects of ternary components on the binary VLE have been studied. 2-Octanone has been selected as oxygenate impurity representative for ketones which are difficult to separate from phenol for its pure component boiling point of  $T_b = 446$  K, which is close to the natural boiling point of phenol ( $T_b = 455$  K). Since the ketones and phenol are typically encountered in complex multicomponent mixtures, the effects of a range of ternary compounds on the VLE behavior of 2-octanone – phenol have been studied. Studies on VLE and other behavior for phenol<sup>9,16</sup> and ketones<sup>17,18</sup> have been reported in literature, but not for the binary combination of 2-octanone-phenol in non-aqueous systems.<sup>19–22</sup>

The enthalpic effects related to the intermolecular interactions occurring in the evaluated mixtures have been determined using isothermal titration calorimetry (ITC). Sprakel et al.<sup>23</sup> showed that ITC can be used to study the interactions for phenol in solvent phases for liquid–liquid extraction. Next to that the combination of ITC and molecular modeling (MM) can be used to study and predict solvent interactions in affinity separation processes.<sup>24,25</sup> For a solvent in an affinity separation process such as extractive distillation, there should be a significant interaction with one of the mixture components that is also substantially different from the interaction with the other mixture component.<sup>24,26</sup> The combination of the VLE data, ITC and molecular modeling (MM) data provides information on phenol interactions with the different ketones in complex multicomponent systems containing close boiling components. The generated molecular interaction insights have been used to steer the selection of a potential entrainer that influences the relative volatility of the phenol – 2-octanone separation sufficiently to avoid the observed azeotrope for this binary mixture.

## MATERIALS AND METHODS

### Chemicals

The chemicals used in this study are listed in Table 1, together with the purity, natural boiling point and supplier. Chemicals were used as received without any further purification.

### Vapor–liquid equilibria (VLE)

Vapor–liquid equilibria (VLE) were measured using a Fischer Labodest VLE602 ebulliometer, with a magnetically stirred equilibrium cell that is heated with an immersion heater and connected to a Cottrell circulation pump. The power supplied to the reboiler, the temperature of the heating mantle and the pressure can be and were set independently. A pressure range between 10 kPa and atmospheric pressure can be used applying an Edwards E2M1.5 vacuum pump. Pt-100 thermocouples were used to measure the equilibrium temperature of the mixture as well as the liquid temperature in the reboiler. Before each experiment, the equilibrium cell was filled with 80 mL of liquid mixture, being either a binary or a ternary mixture. For ternary mixtures, the desired composition of the 2-octanone – phenol mixture was applied in approximately 40 g, and an equal mass of the ternary component was added for  $S/F = 1$  experiments. For experiments with  $S/F$  deviating from unity, the masses of the 2-octanone – phenol mixture and ternary component were changed accordingly, in all cases to yield a total of 80 mL liquid. For each experiment with a different liquid mixture composition, vapor – liquid

equilibrium was generally reached after 30–90 min, indicated by a steady flow of condensed vapor drops, after which samples were taken of both the liquid phase and the condensed vapor phase. As the liquid phase flow is significantly larger than the vapor phase flow, the measured concentration of the liquid phase sample was checked and verified based on the initial feed concentration in all cases. Liquid and vapor phase samples were analyzed for their phenol concentration by GC–MS.

### GC–MS

The samples of the liquid phase and condensed vapor phase after equilibration in the ebulliometer experiments were analyzed with a 7890A Ms 5975C Agilent GC–MS with FID and an Agilent HP-5Ms, HP19191S-433 column with helium as the carrier gas. Samples were dissolved in acetone. The initial temperature of the oven was set to 318 K. During the analysis the oven temperature was increased to 523 K using a linear profile at a heating rate of  $0.25 \text{ K s}^{-1}$ , starting immediately at the start of the analysis.

### ITC

Isothermal titration calorimetry (ITC) experiments were performed using a TA Instruments TAM III micro calorimeter operated in dynamic correction mode. The thermostat temperature was set to 293 K. A set of two 4 mL cells were used as the sample cell and the reference cell. The sample cell was stirred with a golden stirrer at a stirring speed of  $1.33 \text{ s}^{-1}$ . In the reference cell the amount of water was adjusted to ensure that this cell had in total a heat capacity equal to that of the sample cell.

With the ITC measurements, heat of mixing profiles were obtained for the binary mixtures. In some cases, also another solvent component was added. Each titration experiment consisted of 15 injections of  $15 \mu\text{L}$  with an injection interval of  $3.0 \times 10^3 \text{ s}$  to ensure that the signal returned to the baseline. For the first injection only a titration of  $3 \mu\text{L}$  was applied and this data point was not taken into account in further analysis as there may be an effect of diffusive loss of titrant.<sup>27</sup> Two separate titration experiments, i.e. titration of component A to B and vice versa, together form one set of data for the heat of mixing of two components. Because of its relatively high melting point ( $40.5 \text{ }^\circ\text{C}$ ) phenol cannot be applied as a pure component in these experiments. Therefore, ITC experiments for the phenol-2-octanone mixtures were performed by titrating 2-octanone to ( $9.1 \text{ mol}\cdot\text{kg}^{-1}$ ) phenol in 2-octanone and titrating phenol in 2-octanone ( $8.2 \text{ mol}\cdot\text{kg}^{-1}$ ) to 2-octanone. Previous work on ITC for reactions and interactions of this range showed standard deviations of  $<2\%$  in the heat released for reaction enthalpies of above  $15 \text{ kJ}\cdot\text{mol}^{-1}$ , leading to values for the injection heat ranging from approximately  $0.02$ – $2 \text{ J}$ .<sup>28</sup> In this work injection heat ranged from approximately  $0.1$ – $1 \text{ J}$ , so similar low standard deviations are expected.

### Molecular modeling (MM)

Wavefunction's Spartan'18 Parallel software was applied for molecular modeling (MM) of the direct interaction energy of the components of the mixtures studied in this work. In case the molecule was included in Spartan's SSPD database, those geometries were used. Otherwise initial geometries were obtained from molecular mechanics simulation. As a first step, the molecular geometry was optimized for individual molecules using the DFT- $\omega\text{B97X-D-6-31G}^*$  level of calculation and a parametrization assuming a conductor-like polarizable continuum model (CPCM) solvation using a default value of 37 for a high dielectric constant (i.e. a polar solvent). In a second step the ensemble geometry was

**Table 1.** Chemicals used in this study

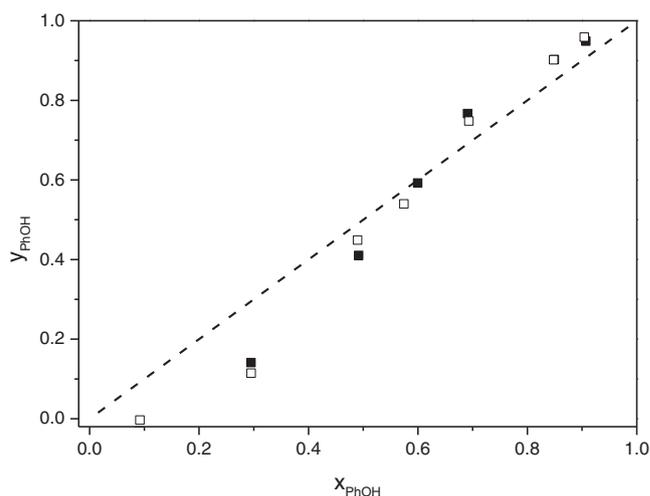
Chemical		Purity/%	Boiling point /K	Provider
acetone	Lichrosolv®	≥99.8	329.2	Merck KGaA/SigmaAldrich
Acetophenone	(AcPhO)	99	475	Merck KGaA/SigmaAldrich
alpha-methylstyrene	(AMS)	98	438–442	Merck KGaA/SigmaAldrich
Cumene	(Cu)	98	425	Merck KGaA/SigmaAldrich
dimethyl benzyl alcohol	(DMBA)	97	475.2	Merck KGaA/SigmaAldrich
Cyclohexane	(CHex)	99.5	353.89	Merck KGaA/SigmaAldrich
Diethylene glycol	(DEG)	>99	471–473	Merck KGaA/SigmaAldrich
diethylene glycol dibutyl ether	(DEGDBE)	≥99	529	Merck KGaA/SigmaAldrich
Dodecane	(DDec)	≥99	489	Merck KGaA/SigmaAldrich
1-dodecanol	(1-DecOH)	≥98%	498	Merck KGaA/SigmaAldrich
Ethylene glycol	(EG)	≥99.8	470	Merck KGaA/SigmaAldrich
Hexadecane	(HexD)	99	560	Merck KGaA/SigmaAldrich
hydroxyethyl ethylene diamine	(heediamine)	99	511–513	Merck KGaA/SigmaAldrich
hydroxy acetone	(HyAc)	≥95	418–419	Merck KGaA/SigmaAldrich
hydroxy acetophenone	(HyAcPhO)	99	569	Merck KGaA/SigmaAldrich
Mesityl oxide	(mes.ox)	98	402.6	Merck KGaA/SigmaAldrich
5-methyl-2-hexanone	(5-m-2-one)	98.0	417	Merck KGaA/SigmaAldrich
methyl isobutyl ketone	(MIBK)	≥99.7	390–391	Merck KGaA/SigmaAldrich
1-octanol	(1-octOH)	≥99	468	Merck KGaA/SigmaAldrich
2-octanone	(2-octO)	98	446	Merck KGaA/SigmaAldrich
1-pentanol	(1-pentOH)	≥99	410 = 412	Merck KGaA/SigmaAldrich
polyethylene glycol (average molar weight 200 g/mol)	(PEG200)	-	>423	Merck KGaA/SigmaAldrich
Phenol	(PhOH)	≥99.5	454.8	Merck KGaA/SigmaAldrich

optimized using the same level of calculation. All calculations were performed in fivefold and the initial positioning of the molecules in the ensemble was randomly varied, to exclude the possibility of calculating local minima. For the final calculation, the average energy minimum was used. For the calculation of solvent effects, binary ensembles were combined with two solvent molecules. In these cases, CPCM was applied to reflect the bulk solvent in the system as well.

## RESULTS AND DISCUSSION

### Binary VLE data of the system 2-octanone– phenol

The binary VLE data of 2-octanone and phenol was studied at pressures of 30 and 100 kPa, see Fig. 1 and Table A2 in the Supplementary Information. These VLE data show a clear maximum boiling azeotrope at both 30 and 100 kPa. This means that at low phenol contents, 2-octanone is the more volatile component, which is to be expected based on the pure component boiling points (446 K versus 455 K for phenol). With increasing phenol content, the relative volatility decreases, which can be ascribed to the hydrogen bond donating character of phenol, and the hydrogen bond accepting character of 2-octanone. By accepting hydrogen bonds from phenol, 2-octanone becomes less volatile, resulting in an azeotropic composition at about  $x_{\text{PhOH}} = 0.6$ . The hydrogen bonding to 2-octanone affects the volatility of phenol to a lesser extent, because phenol already forms intramolecular hydrogen bonds due to its ability to be a hydrogen bond donor as well as a hydrogen bond acceptor. The azeotropic behavior implies that separation of this binary mixture into its pure chemical components by ordinary distillation is impossible and thus

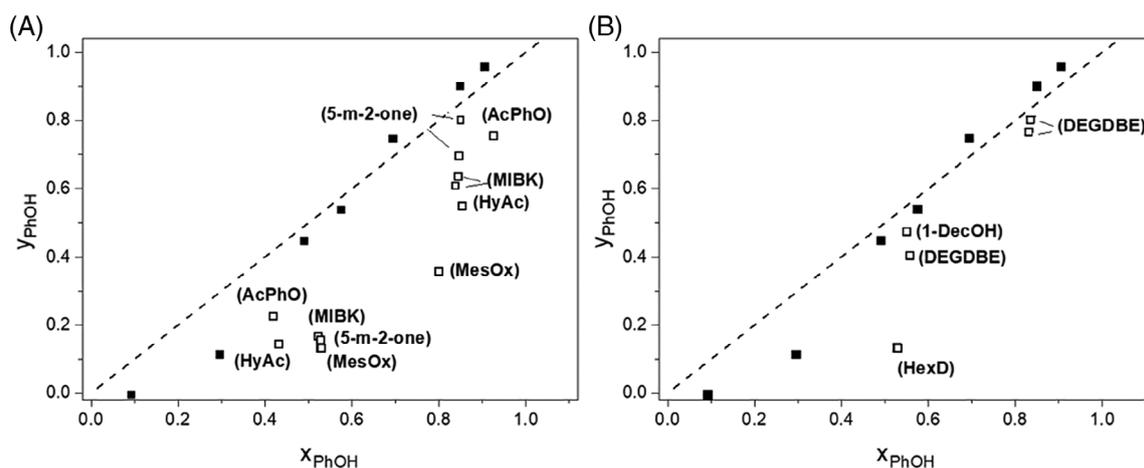


**Figure 1.** Binary VLE data for the system phenol - 2-octanone at 30 (closed) and 100 (open) kPa, equilibrium concentrations are listed in the Supplementary Information Table A2.

other techniques such as extractive distillation (ED) are required to separate this mixture.

### Effect of ternary components on the binary VLE of 2-octanone– phenol

The effect of added ternary components on the VLE for the phenol - 2-octanone mixture was studied to improve fundamental understanding of interactions taking place between phenol, 2-octanone and the ternary component. This improved



**Figure 2.** Binary (closed symbols) and pseudo-binary (open symbols) VLE data for phenol and 2-octanone at 100 kPa, with various solvents at a 1:1 weight based S/F-ratio, showing (a) ketone solvents, (b) alkane, ether, alcohol, aromatic and combined components. Equilibrium concentrations are listed in the Supplementary Information Table A3.

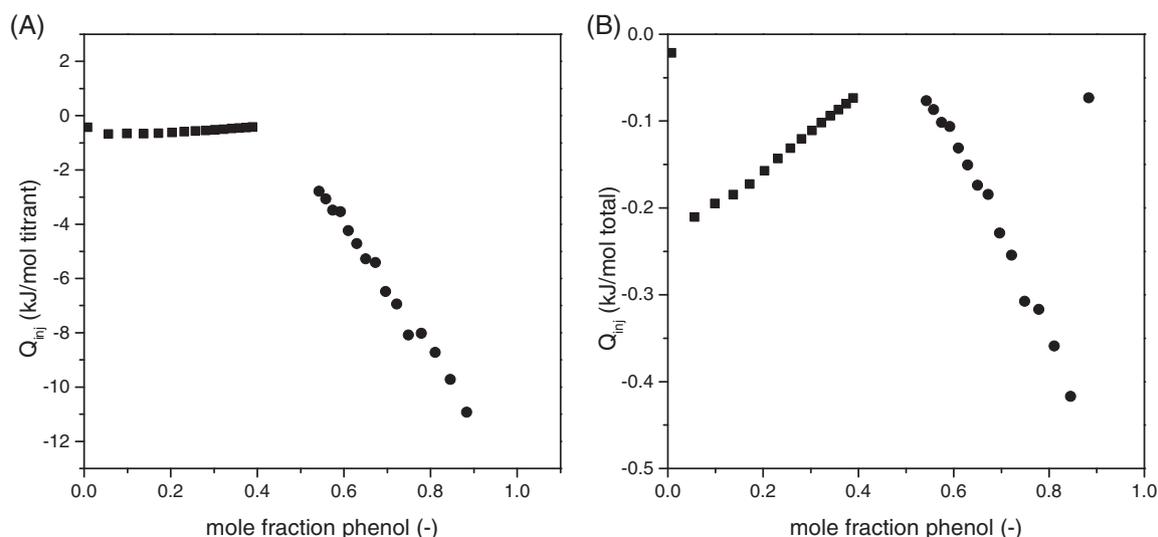
fundamental understanding then guides the selection of a proper solvent to avoid azeotropic behavior for this binary mixture (as will be discussed in one of the next sections). The effect of the investigated ternary components on the binary VLE data of phenol and 2-octanone at 100 kPa is shown in Fig. 2 and Table A3 in the Supplementary Information. Addition of hydroxyethyl-ethylene diamine resulted in a color change of the mixture, indicating that a chemical reaction occurred. Consequently, hydroxyethyl-ethylene diamine is regarded as an unsuitable solvent and the component is not represented in Fig. 2. The high reactivity of this component is probably due to its strong basicity (as expected based on the high  $pK_{\text{BH}^+}$  and  $pK_{\text{B}^-}$  of ethylene diamine and other diamines.<sup>29</sup>

Figure 2(a) shows ketone type solvents, of which some have additional functional groups like an aromatic, an alcohol or a double bond functionality. These components are low boiling (higher volatility) compared to the binary mixture, except for acetophenone. Comparing among the (low-boiling) ketone components shows that the larger ketones perform slightly worse in affecting the relative volatility than the small molecule MIBK, which might be a result of the influence of London dispersion forces for larger (chain) molecules. However, since MIBK has a lower molar weight, the higher molar ratio MIBK: 2-octanone can certainly also play a role, as more MIBK-phenol interactions block the similar interaction for 2-octanone. For the high-boiling component acetophenone a positive effect on the 2-octanone and phenol relative volatility is observed, although in general less than for the low boiling ketones, in line with the observed trend for low-boiling ketones. However, at high phenol fraction of the binary mixture the difference between acetophenone and the smaller ketones is less significant. The relatively poor effect of acetophenone could be a result of the presence of the aromatic group or due to London dispersion forces that reduce the effect of the functional (ketone) group. When cumene, also an aromatic component, was applied the relative volatility of 2-octanone over phenol strongly reduced (not shown in graph). A possible explanation for this effect is that the addition of cumene leads to the occurrence of  $\pi\pi$ -interactions between cumene and phenol. Although typically less strong than the combination of the H-bonding and  $\pi\pi$ -interactions occurring between multiple molecules of phenol, there will be a statistical distribution among the

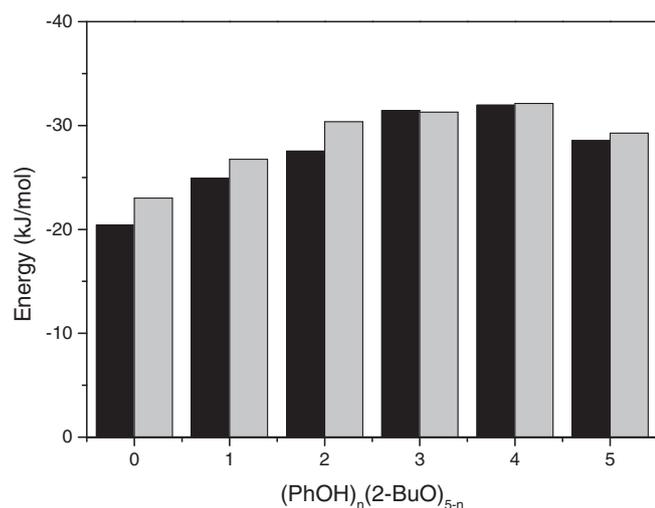
different intermolecular interactions, resulting in a net reduction of the phenol-phenol interactions. This would result in a higher volatility of phenol. Similar  $\pi\pi$ -interactions were observed by Zhao et al. for the benzene – phenol system.<sup>30</sup> The occurrence of these types of intramolecular interactions for phenol seem to be confirmed by ITC measurements and MM calculations, as will be discussed later. Figure 2(b) shows the effects of other components such as alcohols, ethers, aromatic components, alkanes and components with combinations of these functional groups. These components are all high-boiling compared to the binary mixture. Application of the alkane results in a strong effect on the relative volatility (especially when focusing on the lower phenol fraction in the binary mixture), especially when compared to the alcohols and ether with longer carbon chains in the molecule. In general, there is a strong effect of the alkane, probably as a result of positive deviations from Raoult's law, followed by the aromatic ketone, the ether and the alcohol. All evaluated components, apart from cumene and hexadecane, are apparently (marginally) stronger hydrogen bond acceptors from phenol than 2-octanone, as indicated by the  $\text{BF}_3$ -affinities of the ketones compared to 2-octanone,<sup>29</sup> increasing the relative volatility of 2-octanone over phenol. The positive effect of 1-DecOH, most likely a less strong Lewis base than 2-octanone based on  $pK_{\text{BH}^+}$  values of very similar alcohols and ketones,<sup>29</sup> is probably due to the improved total mole fraction of Lewis bases in relation to the phenol mole fraction. This effect also plays a role for the influence of added ketones on 2-octanone – phenol VLE.

#### Interactions in the system 2-octanone– phenol studied with ITC and molecular modeling (MM)

Figure 3(a) shows the heat release from titrating 2-octanone to (9.1 mol·kg<sup>-1</sup>) phenol in 2-octanone (circles) and titrating phenol in 2-octanone (8.2 mol·kg<sup>-1</sup>) to 2-octanone (squares). There is a weak exothermic heat of injection for all compositions measured, which is more exothermic at high phenol fractions. Since mixing is more exothermic at higher phenol fractions, this suggests that phenol forms preferably larger complexes with other phenol complexes that have, on average, overall stronger bonds than at low concentration. This is most probably a result of strong  $\pi\pi$ -interactions in combination with the formation of intramolecular hydrogen bonds (since phenol is a hydrogen bond donor and



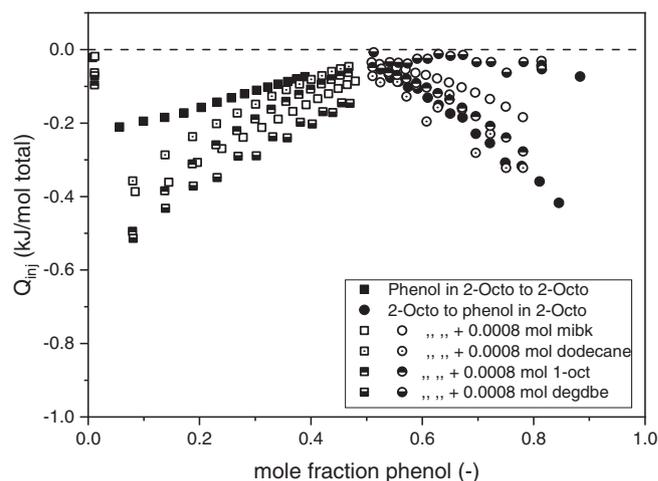
**Figure 3.** (a) Heat of injection ( $\text{kJ}\cdot\text{mol}^{-1}$  titrant) from titrating phenol in 2-octanone ( $8.2\text{ mol}\cdot\text{kg}^{-1}$ ) to 2-octanone (squares) and titrating 2-octanone to ( $9.1\text{ mol}\cdot\text{kg}^{-1}$ ) phenol in 2-octanone (circles), and (b) Heat of mixing ( $\text{kJ}\cdot\text{mol}^{-1}$  total) in the sample) of phenol in 2-octanone ( $8.2\text{ mol}\cdot\text{kg}^{-1}$ ) to 2-octanone (squares) and titrating 2-octanone to ( $9.1\text{ mol}\cdot\text{kg}^{-1}$ ) phenol in 2-octanone (circles).



**Figure 4.** Energy of complex formation (kJ per molecule in the complex) between  $n$  phenol molecules and  $(5-n)$  molecules of 2-BuO, without (black) and with (grey) presence of 2 molecules of the solvent MIBK, calculated with Wavefunction's Spartan'18 Parallel.

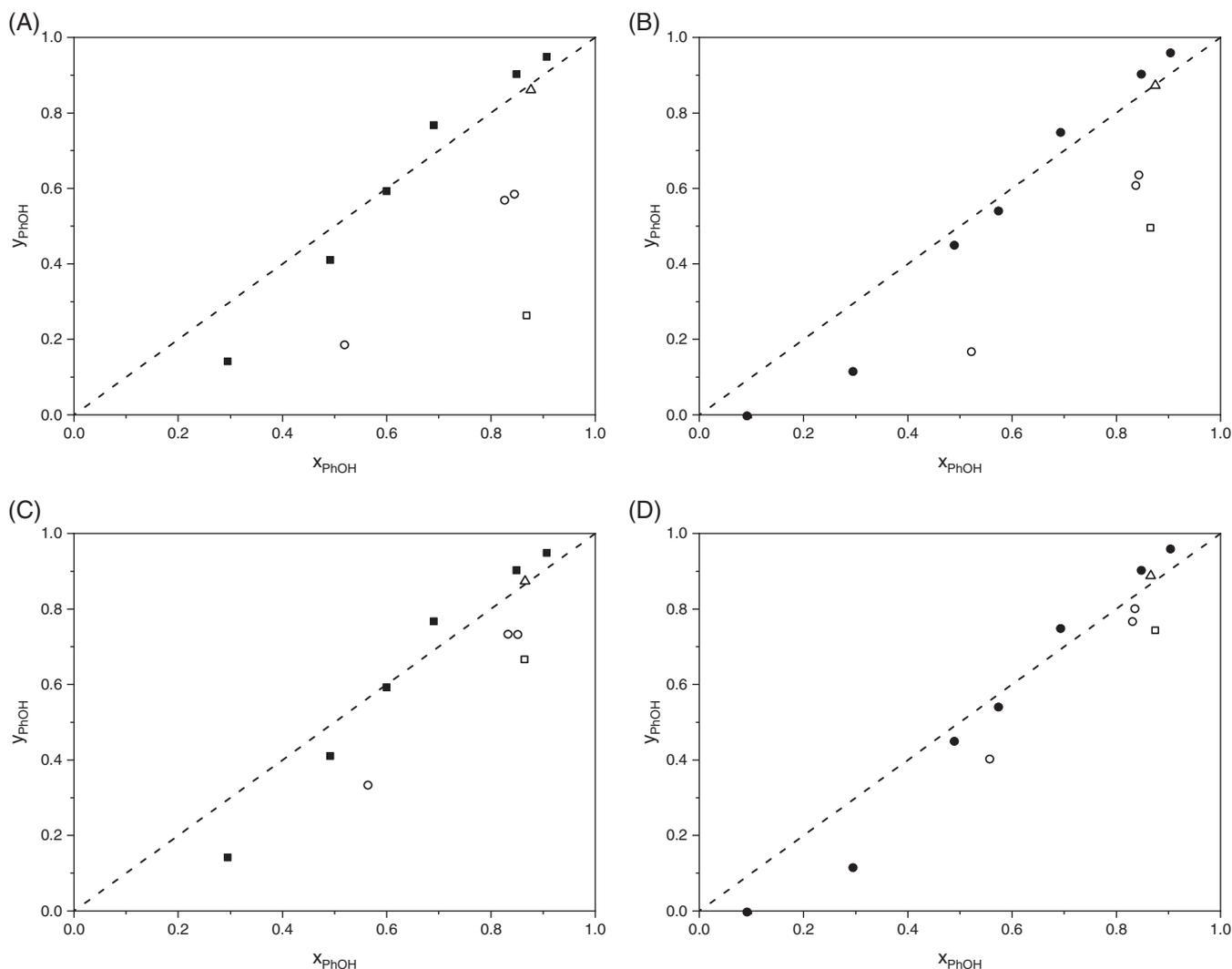
acceptor). Similar large complexes with multiple types of interaction varying based on the composition of the mixture have also been reported for nonylphenol.<sup>31</sup> At very low phenol fraction also an exothermic heat of mixing is observed, as a result of hydrogen bonding between phenol and 2-octanone. Figure 3(b) shows these results expressed as the heat of mixing per total amount of moles present in the system, from which the more pronounced exothermic heat effect of mixing for asymmetric mixtures is evident. The results at low phenol fractions imply that the bond between 2-octanone and phenol is (marginally) stronger than the phenol-phenol bond, apart from the interaction between larger complexes as mentioned earlier.

The heat effects and intermolecular interactions at low and high phenol fraction were further studied with molecular modeling



**Figure 5.** Heat of mixing of phenol and 2-octanone, obtained from (squares) titrating a  $8.2\text{ mol}\cdot\text{kg}^{-1}$  phenol solution to approx.  $0.0021\text{ mol}$  2-octanone and (circles) titrating 2-octanone into approximately  $0.003\text{ mol}$  of  $8.2\text{ mol}\cdot\text{kg}^{-1}$  phenol solution. In the cases with an additional solvent,  $0.0008\text{ mol}$  of the solvent was added to the sample. The mole fraction of the solvent in the phenol 2-octanone mixture is (depending on the experiment) between  $0.2$ – $0.3$  before titration, and approximately  $0.1$  after the titration experiment.

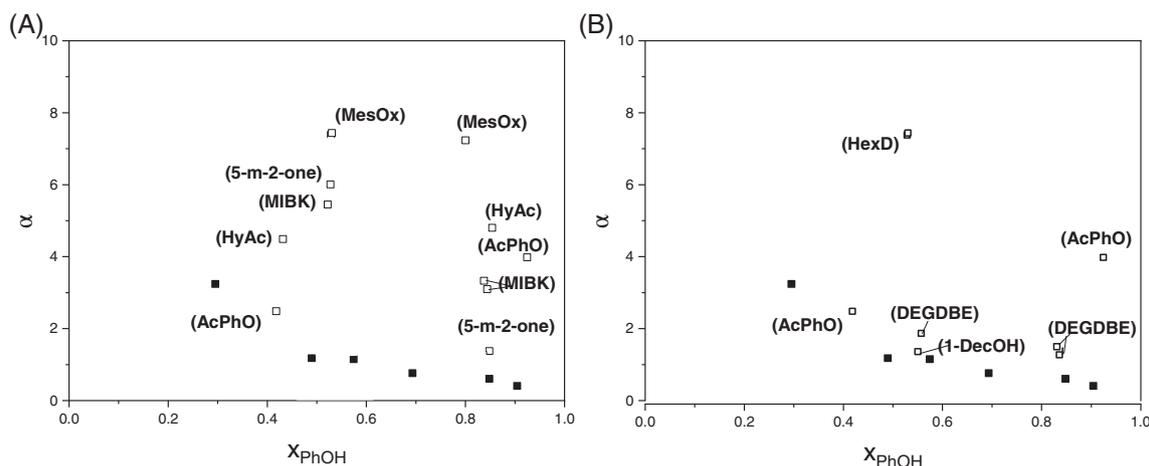
(MM). For the molecular modeling of the ensembles formed between phenol and 2-octanone, it was chosen to use 2-butanone as a model compound (representing 2-octanone), to improve the calculation speed. Complexes of phenol and 2-butanone were also modeled in fivefold using Wavefunction's Spartan'18 Parallel molecular modeling software, see Fig. 4. In this case, complex formation is clearly stronger for complexes with a higher phenol fraction. This strongly supports the findings in ITC that a more pronounced exothermic heat of mixing is found especially at higher phenol fractions. Considering these effects at low and high phenol concentration, strong non-ideality in the mixture can be expected, thereby supporting the measured VLE data of the binary mixture in which an azeotrope was observed, see Fig. 1.



**Figure 6.** Effect of weight based S/F-ratio ( $\circ$  S/F = 1,  $\triangle$  S/F = 0.33 and  $\square$  S/F = 3), system pressure and solvent type on binary (closed) and pseudo-binary (open) VLE data of the system 2-octanone over phenol. The applied solvents are (a + b) the ketone MIBK and (c + d) the ether DEGDBE, at a pressure of (a + c) 30 kPa and (b + d) 100 kPa.

The effect of solvent addition on the heat of mixing of the binary system phenol– 2-octanone was also measured in ITC, see the results in Fig. 5. All measured heats of mixing were exothermic, although for DEGDBE at higher phenol fractions, the effect is marginal. Interpretation of the heat effects requires considering that due to the melting point of phenol, it cannot be applied purely, neither in the measurement cell, nor as titrant. Therefore, although in high phenol mole fractions, phenol is always present in diluted form. In general, it can be concluded from the results in Fig. 5, that the effect of a solvent at low phenol fractions and at high phenol fractions is different, and even opposite. Organizing the solvents in the order of increasing heat of mixing at low phenol fractions, the same range of solvents show a reasonably decreasing trend in the heat of mixing at high phenol fractions. This opposite trend may be explained by considering that for the measurements at low phenol composition, the phenol concentration in the titrant is high, while the concentration of phenol in the measurement cell is low, while for measurements at high phenol concentration, the opposite is true, i.e. the concentration of phenol in the titrant is low and the concentration

phenol in the measurement cell is high. The large number of intermolecular interactions and high level of complexation in highly concentrated phenol titrant will result in breaking of at least a fraction of these interactions upon titration, while simultaneously new bonds are formed, possibly also with the solvents. The observed heat of mixing depends on the nature of the solvent, and thus on the interactions it can form with phenol. For solvents where the interaction is stronger, this results in larger heat of mixing, whereas for the same solvent at high phenol fractions, these interactions are already present in the sample cell mixture, and dilution with 2-octanone affects these interactions less. DEGDBE and 2-octanone are not capable of hydrogen bond formation when pure, since they only have hydrogen bond accepting groups. As a result of a stronger interaction with phenol than with 2-octanone, at high phenol fraction the solvent effect is small whereas at low phenol fraction DEGDBE is the strongest competitor for interaction and the heat of mixing in presence of DEGDBE is larger exothermic. When the solvent has less strong interactions with phenol, e.g. in the case of the apolar dodecane that is not capable of forming hydrogen bonds or  $\pi\pi$ -interactions, the



**Figure 7.** Binary (closed symbols) and pseudo-binary (open symbols) relative volatility data for 2-octanone over phenol at 100 kPa with various solvents at a 1:1 weight based S/F-ratio, showing (a) ketone solvents, (b) alkane, ether, alcohol, aromatic and combined components.

solvent effect is marginal for all compositions. Concluding, based on these ITC results, the interaction is most strong with DEGDDBE, followed by MIBK, 1-octanol and dodecane. Compared with VLE measurements, also a stronger effect was seen for MIBK and DEGDDBE, followed by a similar alcohol 1-dodecanol.

Figure 4 also shows that in this case the addition of two molecules of the solvent MIBK (grey bars), increases the overall exothermic interaction energy of the complex (5 + 2 solvent molecules), but does not increase the interaction energy per molecule in the complex strongly. This supports the ITC findings for the system of 2-octanone and phenol, where addition of MIBK did not affect the energy of mixing strongly (see results in Fig. 5, which will be explained later in this section). A possible explanation for the difference in observation for MIBK in ITC and MM compared to VLE is that the VLE experiments were conducted at higher solvent to feed ratios than used in ITC and the MM calculations, and VLE experiments at lower solvent to feed ratio also showed lower effects of the solvent on the 2-octanone – phenol relative volatility as will be discussed later in this manuscript. Moreover, the same trend of energy of complex formation with ensemble composition is visible for the cases with and without solvent. This indicates that there are no specific interactions between the binary mixture and the solvent molecules that affect the heat of mixing.

#### Effect of S/F-ratio on VLE data of 2-octanone – phenol

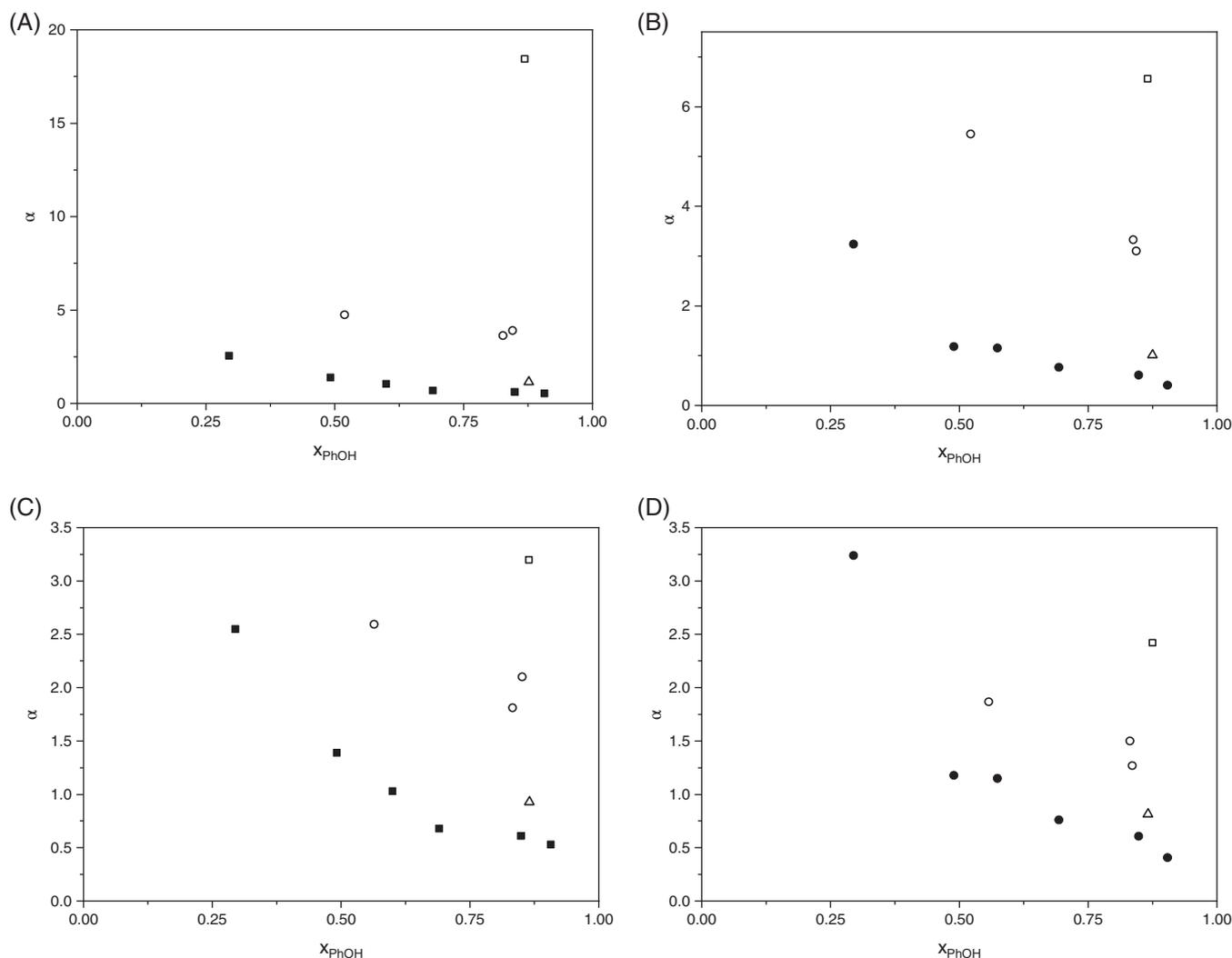
The effect of the S/F-ratio on the VLE data of 2-octanone – phenol is stronger for low-boiling ketones (such as MIBK) than for the high-boiling ether (diethylene glycol dibutyl ether, DEGDDBE), see Fig. 6. Especially at higher S/F-ratio the effect of MIBK is significantly stronger than that of DEGDDBE, an effect that is less pronounced at 100 kPa (Fig. 6b). A possible explanation may be that the ketone group is more polar than the ether group. Another option is that there is a difference in the effect of the S/F-ratio on the vapor and liquid fractions of the solvent, since MIBK is a low-boiling component with relatively high presence in the vapor phase whereas DEGDDBE is a high-boiling component with relatively high presence in the liquid phase of the ternary mixture. Although it could be expected that increasing the S/F-ratio has more effect on the liquid fraction of MIBK, the weight fraction of MIBK in the liquid phase samples was checked and did not show a more than proportional increase with increasing S/F-ratio.

#### Binary and ternary VLE data for other oxygenate – phenol systems

To validate whether conclusions drawn for 2-octanone are also applicable for other oxygenates in mixtures with phenol, three binary mixtures of phenol with components with other functional groups were studied, a mixture of phenol with hydroxy acetone, with mesityl oxide and with 1-pentanol. Binary VLE-data as well as pseudo-binary VLE data are shown in the Supplementary Information. For hydroxy acetone binary VLE data (Fig. A1) with a tangent pinch at high phenol fractions was measured. The relative volatility for this mixture could be strongly improved by the addition of ketones and ethers. It is thus shown that the presence of an impurity in the mixture may solve the challenge of an azeotrope in the phenol containing solution. For the binary mixture of phenol with mesityl oxide (Fig. A2(a)) and the binary mixture of phenol with 1-pentanol (Fig. A2(b)), the binary VLE data show almost ideal VLE behavior, and also show a high relative volatility with small solvent (impurity) effects as a result of that. For the mixture of 1-pentanol – phenol only the most apolar solvent dodecane reduced the relative volatility, whereas for the binary mixture mesityl oxide – phenol only the apolar cumene clearly reduced the mesityl oxide – phenol relative volatility. In general, for all binary systems with phenol, polar and hydrogen bond accepting groups and linear alkanes (repelling molecules) increase the relative volatility of the other component over phenol, whereas apolar aromatic group containing solvents either decrease the relative volatility or have marginal or no effect. The increase of relative volatility is in these cases based on hydrogen bonding between the solvent and phenol or stronger repelling behavior (positive deviations from Raoult's law) for the ketone than for the more hydrophobic phenol molecule.

#### Effects on selection of solvents for extractive distillation

For application of solvents in an extractive distillation (ED) process, next to characteristics of such solvent, cost, environmental impact and reactivity, the boiling point of the solvent and especially the difference in boiling point with that of the components of the binary mixture that is to be separated is crucial. For a process of separating the azeotropic binary mixtures of 2-octanone and phenol by ED, solvents with specific types of functional groups, i.e. ketones, ethers or alkanes appear promising, based on the results in Figs 2 and 6. Based on these results, for 2-



**Figure 8.** Effect of weight based S/F-ratio ( $\circ$  S/F = 1,  $\triangle$  S/F = 0.33 and  $\square$  S/F = 3), system pressure and solvent type on binary (closed) and pseudo-binary (open) relative volatility  $\alpha$  of the system 2-octanone over phenol. The applied solvents are (a + b) the ketone MIBK and (c + d) the ether DEGDBE, at a pressure of (a + c) 30 kPa and (b + d) 100 kPa.

octanone – phenol, either addition of hydrogen bond accepting or polar ternary compounds can improve the relative volatility, as well as the addition of an apolar alkane solvent that induce positive deviations from Raoult's law.

For a more clear comparison, Fig. 7 shows the (pseudo-)binary VLE data of Fig. 2, expressed as the relative volatility of phenol of 2-octanone, with ketone solvents in Fig. 7(a) and other components in Fig. 7(b). Also in these figures the effect of the low-boiling ketones, the high-boiling acetophenone (AcPhO), the ether DEGDBE and the alkane hexadecane (HexD) is clear. A relative volatility of 2-octanone over phenol of 2–6, depending on the composition and specific case, is obtained for most cases, making these solvents potentially interesting for application in an ED process.<sup>32</sup>

The results on the (pseudo-) binary VLE data of Fig. 6 were also presented as the relative volatility of 2-octanone over phenol in Fig. 8. The stronger effect of addition of MIBK compared to DEGDBE is also clear for these cases. However, as MIBK is a low-boiling component, for application in an ED process out of these two only DEGDBE is suitable. For application of DEGDBE the relative volatility increased to values significantly in excess of 1 and

for S/F > 1 the relative volatility is even in excess of three in all cases, making DEGDBE a potentially interesting solvent for application in an ED process. Optimizing the solvent choice and operational specifications would require further investigation of potential solvents and the effect of S/F-ratio of other high boiling ketones and linear alkanes.

Based on the observed interaction effects, high-boiling ketones, ethers or alkanes are suggested as potentially successful solvents for ED processes to recover phenol from complex mixtures containing ketones with similar boiling points, next to other compounds.

## CONCLUSION

Separation of 2-octanone from phenol by distillation is challenging as a result of the azeotropic behavior. Addition of other ketones, ethers or alcohols can have a strong effect on the VLE data. The binary system of 2-octanone and phenol already comprises of a complex set of intermolecular interactions, including hydrogen bonding and  $\pi\pi$ -interactions, and adding solvents with hydrogen bond accepting behavior affects the binary

interactions. For some solvents the affinity for hydrogen bonding with phenol is stronger than for 2-octanone, but also for other solvents with lower hydrogen bonding capacity, their addition improves the relative volatility and breaking the azeotrope due to interference with intermolecular interactions in the binary system, and competitive hydrogen bonding. Especially at higher S/F-ratio the effect of the ketone MIBK is strong. A similar but smaller effect was observed for the ether DEGDBE. Using ITC, supported by MM, showed a more exothermic heat of injection for 2-octanone – phenol mixtures at high phenol fractions, suggesting formation of larger complexes with on average stronger bonds. The use of larger S/F-ratios of hydrogen bond accepting solvents reduces the phenol fraction significantly, and thereby interferes in the complex formation. In effect, the solvents then compete with 2-octanone for the hydrogen bonds with single phenol molecules and smaller complexes, resulting in breaking of the azeotrope.

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## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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