Supporting Information on Thermophysical Properties of Mixtures of Titanium(IV) Isopropoxide (TTIP) and 2-Propanol (iPOH)

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1. Physico-chemical VLE model of TTIP + iPOH

The model used in the present work for describing the VLE data in the system TTIP + iPOH is a physico-chemical model in which the following hetero-dimerization of TTIP and iPOH in the vapor phase is considered:

\[
\text{TTIP} + \text{iPOH} \rightleftharpoons \text{TTIP·iPOH} ,
\]

(SI)

while no chemical reactions are considered in the liquid phase. We do not claim that this model is based on a realistic physico-chemical picture; the choice was made only on empirical grounds to obtain a reasonable description of the VLE data from the present work, as described in the main text.

The three components in the vapor phase are assumed to form a mixture of ideal gases. The chemical equilibrium constant of the hetero-dimerization is

\[
K^1 = \frac{y_{\text{TTIP·iPOH}}^* P^0}{y_{\text{TTIP}}^* y_{\text{iPOH}}^* P} ,
\]

(S1)

where \( P^0 = 100 \) kPa. \( K^1 \) is an adjustable model parameter.

The phase equilibrium is described by

\[
p_i^s \cdot x_i \cdot y_i^* = p \cdot y_i^* \quad \quad i = (\text{TTIP}, \text{iPOH})
\]

(S2)
where $p_i^s$ is the vapor pressure of the pure component $i$, $\gamma_i$ is the activity coefficient of component $i$ in the liquid phase, and $p$ is the pressure. Moreover, $x_i$ is the mole fraction of component $i$ in the liquid phase (where no distinction between the true and the overall mole fraction is necessary), while $y_i^*$ is the true mole fraction of component $i$ in the vapor phase, which is related to the corresponding overall mole fraction $y_i$ by:

$$y_i = \frac{y_i^* + y_{TIP,iPOH}^*}{y_{TIP}^* + y_{iPOH}^* + 2y_{TIP,iPOH}^*} \quad i = (TIP, iPOH)$$  \hspace{1cm} (S3)

As indicated, the phase equilibrium condition Eq. (S3) only applies to TIP and iPOH, as the hetero-dimer is present only in the vapor phase.

The vapor pressures $p_i^s$ of the pure components $i$ are modeled with the Antoine equation

$$\ln(p_i^s / \text{kPa}) = A_i - \frac{B_i}{T / \text{K} + C_i} ,$$  \hspace{1cm} (S4)

where $T$ is the temperature in K and $A_i$, $B_i$ and $C_i$ are adjustable parameters.

The non-ideality of the mixture of the two components in the liquid phase is described by the NRTL model:

$$\ln \gamma_i = x_j^2 \left[ \frac{G_{ji}}{x_i + x_j \cdot G_{ji}} \right]^2 + \frac{\tau_{ji} G_{ji}}{(x_j + x_i \cdot G_{ji})^2} ,$$  \hspace{1cm} (S5)

where

$$\ln G_{ij} = -a_{ij} \cdot \tau_{ij} .$$  \hspace{1cm} (S6)
The three NRTL parameters $\tau_{ij}$, $\tau_{ji}$ and $\alpha_{ij} = \alpha_{ji}$ are adjusted the VLE data, together with $K^l$.

2. **Comparison of experimental data for pure iPOH to literature data**

In this section, the experimental data of the density, viscosity, thermal conductivity and isobaric heat capacity of pure 2-propanol (iPOH) from the present work are compared to literature data.
2.1 Density

A comparison of density data of pure iPOH from the present work and literature values\(^1\text{--}^{23}\) is presented in Figure S1. Figure S1 shows that the relative deviation \(d_r\) of the results from the present work to the mean of all cited data is \(d_r(\rho) \leq 0.0002\).

![Figure S1: Relative deviation of experimental densities \(\rho\) from the present work to literature values\(^1\text{--}^{23}\) for pure iPOH. The experimental uncertainties are shown only for the data from the present work. \(\tilde{\rho}\) is a temperature-dependent quadratic fit to all cited literature sources.](image)
2.2 Viscosity

A comparison of viscosity data of pure iPOH from the present work and literature values $3^{–5,24–30}$ is presented in Figure S2. Figure S2 shows that the relative deviation of the results from the present work to the mean of all cited data is $d(\eta) \leq 0.025$, except for 333.15 K. The higher deviation observed at 333.15 K results from the large deviation of the data by Kermanpour et al. to the other sources. When ignoring these values, the relative deviation of our data point to the average of the remaining sources reduces to $d(\eta) \leq 0.018$ at 333.15 K.

Figure S2: Relative deviation of experimental viscosities $\eta$ from the present work to literature values $3^{–5,24–30}$ for pure iPOH. The experimental uncertainties are shown only for the data from the present work. $\bar{\eta}$ is the average viscosity of the cited literature sources which is evaluated separately for each temperature.
2.3 Thermal conductivity

A comparison of thermal conductivity data of pure iPOH from the present work and literature values\textsuperscript{31–34} is presented in Figure S3. Figure S3 shows that the relative deviation of the results from the present work to the data of Ogiwara et al.\textsuperscript{34} is $d_r(\lambda) \leq 0.027$, and that most of the other literature data are within the standard uncertainty of the present work.

Figure S3: Absolute deviation of experimental thermal conductivities $\lambda$ from the present work to literature values\textsuperscript{31–34} for pure iPOH. The experimental uncertainties are shown only for the data from the present work. $\overline{\lambda}$ is a temperature-dependent linear fit to the data of Ogiwara et al.\textsuperscript{34}.
2.4 Isobaric heat capacity

A comparison of isobaric heat capacity data of pure iPOH from the present work and literature values\textsuperscript{35–39} is presented in Figure S4. Figure S4 shows that the relative deviation of the results from the present work to the mean of all cited data is $d_r(c_p) \leq 0.035$ for 293.15 and 313.15 K and $d_r(c_p) \leq 0.085$ for 333.15 K.

![Figure S4: Relative deviation of experimental isobaric heat capacities $c_p$ from the present work to literature values\textsuperscript{35–39} for pure iPOH. The experimental uncertainties are shown only for the data from the present work. $\bar{c}_p$ is the average heat capacity of the cited literature sources which is evaluated separately for each temperature.](image-url)
3. Excess properties of mixtures of TTIP + iPOH

Figure S5 shows the experimental data of the molar excess volumes $v^E$ of mixtures of TTIP + iPOH obtained in the present work together with the correlations presented in the main text. The molar excess volumes are quite small. They are positive for low temperatures and decrease with increasing temperature. As a result, at the highest temperature considered in this work, the molar excess volumes are close to zero for the entire composition range. The correlations describe the experimental data within the standard uncertainty.

![Figure S5](image)

Figure S5: Molar excess volumes $v^E$ of mixtures of TTIP + iPOH at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the experimental standard uncertainty. Lines result from an empirical correlation, cf. Eq. (1) of the main manuscript.
Figure S6 shows the experimental data of the excess viscosities $\eta^E$ of mixtures of TTIP + iPOH obtained in the present work together with the correlations presented in the main text. The excess viscosities are negative for all temperatures. The absolute value of the excess viscosity decreases with increasing temperature.

![Excess viscosities $\eta^E$ of mixtures of TTIP + iPOH at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the experimental standard uncertainty. Lines result from an empirical correlation, cf. Eq. (1) of the main manuscript.](image-url)
4. Thermal diffusivity of mixtures of TTIP + iPOH

Figure S7 shows the experimental data of the thermal diffusivity $\alpha$ of mixtures of TTIP + iPOH obtained in the present work together with the correlations, which can be obtained from combining the correlations of the thermal conductivity $\lambda$, heat capacity $c_p$ and density $\rho$ presented in the main text. The thermal diffusivity increases with increasing amount of TTIP and with decreasing temperature. The correlations describe the experimental data well.

Figure S7: Thermal diffusivity $\alpha$ of solutions of TTIP + iPOH at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the experimental standard uncertainty. Lines are calculated from the empirical correlations presented in the main text.
5. Vapor-liquid equilibrium at 30 – 70 kPa

The experimental data of the VLE in the system TTIP + iPOH are shown together with two different model versions in Figures S8 – S12 for 30 – 70 kPa. In these figures, the solid lines indicate the model for which the NRTL parameters and the equilibrium constant of the hetero-dimerization reaction were fit to the experimental data. The dotted lines indicate the model with the same NRTL parameters, but where the hetero-dimerization reaction in the vapor phase is turned off.

Figure S8: Vapor-liquid equilibrium of the system TTIP + iPOH at 30 kPa. Symbols are experimental data, solid lines are results from the model described in Section 1 of this Supporting Information for which $K^i$ is fit to the experimental data, dotted lines are results from the same model with $K^i = 0$ instead, i.e. no reaction takes place in the vapor phase. The model parameters are given in Tables 10 and 11 in the main manuscript.
Figure S9: Vapor-liquid equilibrium of the system TTIP + iPOH at 40 kPa. Symbols are experimental data, solid lines are results from the model described in Section 1 of this Supporting Information for which $K^3$ is fit to the experimental data, dotted lines are results from the same model with $K^3 = 0$ instead, i.e. no reaction takes place in the vapor phase. The model parameters are given in Tables 10 and 11 in the main manuscript.
Figure S10: Vapor-liquid equilibrium of the system TTIP + iPOH at 50 kPa. Symbols are experimental data, solid lines are results from the model described in Section 1 of this Supporting Information for which $K^I$ is fit to the experimental data, dotted lines are results from the same model with $K^I = 0$ instead, i.e. no reaction takes place in the vapor phase. The model parameters are given in Tables 10 and 11 in the main manuscript.
Figure S11: Vapor-liquid equilibrium of the system TTIP + iPOH at 60 kPa. Symbols are experimental data, solid lines are results from the model described in Section 1 of this Supporting Information for which $K^3$ is fit to the experimental data, dotted lines are results from the same model with $K^3 = 0$ instead, i.e. no reaction takes place in the vapor phase. The model parameters are given in Tables 10 and 11 in the main manuscript.
Figure S12: Vapor-liquid equilibrium of the system TTIP + iPOH at 70 kPa. Symbols are experimental data, solid lines are results from the model described in Section 1 of this Supporting Information for which $K^d$ is fit to the experimental data, dotted lines are results from the same model with $K^d = 0$ instead, i.e. no reaction takes place in the vapor phase. The model parameters are given in Tables 10 and 11 in the main manuscript.
References


(6) Daoudi, H.; Ait-Kaci, A.; Tafat-Igoudjilene, O. Volumetric Properties of Binary Liquid Mixtures of Alcohols with 1,2-Dichloroethane at Different


(13) Gonzalez, B.; Dominguez, A.; Tojo, J. Viscosities, Densities and Speeds of Sound of the Binary Systems: 2-Propanol with Octane, or Decane, or Dodecane.


Propanol, 2-Propanol, 1-Butanol, And 2-Butanol) at (293.15, 298.15, 303.15, 313.15, and 323.15) K. *J. Chem. Thermodyn.* **2008**, *40* (4), 592–598.


(26) Kermanpour, F.; Niakan, H. Z.; Sharifi, T. Density and Viscosity Measurements of Binary Alkanol Mixtures from (293.15 to 333.15) K at


(39) Gómez-Álvarez, P.; González-Salgado, D.; Bazile, J.-P.; Bessieres, D.; Plantier, F. Excess Second-Order Thermodynamic Derivatives of the \{2-Propanol+water\} System from 313.15 K to 403.15 K up to 140 MPa.