Thermophysical Properties of Mixtures of Titanium(IV) Isopropoxide (TTIP) and *p*-Xylene

Alexander Keller^a, Irenäus Wloka^b, Maximilian Kohns^{a,1}, Hans Hasse^a

^a *University of Kaiserslautern, Laboratory of Engineering Thermodynamics (LTD),
Erwin-Schrödinger-Str. 44, D-67663 Kaiserslautern, Germany*

^b *University Duisburg-Essen, Fluid Dynamics, Institute for Combustion and Gas Dynamics,
Carl-Benz-Str. 199, D-47057 Duisburg, Germany*

Abstract

Titanium(IV) isopropoxide (TTIP) is an important precursor for the production of nanoparticles by spray flame processes. In these processes, the precursor is provided in a solution in a combustible solvent, which is *p*-xylene here. As no thermophysical data for solutions of TTIP in *p*-xylene were available in the literature, they were measured in the present work. The vapor-liquid equilibrium was measured at pressures ranging from 20 to 80 kPa. The specific density, viscosity, thermal conductivity, molar isobaric heat capacity, and self-diffusion coefficients were determined experimentally at 101.3 kPa at temperatures between 293.15 and 373.15 K. Sample compositions cover the range from pure TTIP to pure *p*-xylene. Chemical reactions in the studied system were considered. The experiments were carried out in a way that they do not compromise the results for the thermophysical properties. The vapor-liquid equilibrium data were correlated using the NRTL model. Empirical correlations were established for the other properties. The results provide a rational basis for spray flame process design.

Keywords: spray flame synthesis, thermal conductivity, vapor-liquid equilibrium, NRTL, diffusion coefficients

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¹Corresponding author; maximilian.kohns@mv.uni-kl.de

1. Introduction

Titanium(IV) isopropoxide ($\text{Ti}(\text{O}(\text{CH}_3)_2\text{CH})_4$, TTIP) is an interesting precursor for the production of TiO_2 nanoparticles in the spray flame process [1–3]. In the spray flame process, the precursors are dissolved in a combustible solvent and then sprayed into the hot atmosphere of a pilot flame, in which they evaporate and burn. The reactions in the flame lead to the formation of metal oxide nanoparticles. In contrast to the pure gas-phase process route, the choice of the nanoparticle precursor is not limited by its vapor pressure. Instead, the spray droplet formation and characteristics, their secondary breakup and evaporation and the transport processes within the droplet during combustion impact the product properties. In consequence, the quality and the properties of the produced nanoparticles depend strongly on the thermophysical properties of the precursor solutions [1]. Accordingly, thermophysical data on the precursor solutions are needed for the spray flame process design, namely as a basis for process modeling and simulations [1,4–8]. In particular, information on the vapor-liquid equilibrium (VLE), density, viscosity, thermal conductivity, isobaric heat capacity, and diffusion coefficients of the studied precursor + solvent mixtures has to be available. Despite the high interest in spray flame nanoparticle synthesis from TTIP solutions, thermophysical data are only available for pure TTIP and pure combustible solvents, but not for their mixtures. Recent attempts to introduce a standardized synthesis setup within the SpraySyn initiative [9] provide further motivation to investigate the thermophysical properties of precursor solutions.

TTIP is a metal alkoxide which is a liquid at ambient conditions. Bradley et al. [10] give an overview of metal alkoxides. Besides synthesis routes and chemical

properties, they provide information on thermophysical properties of the pure metal alkoxides, such as density and viscosity at ambient conditions. Thomas and Davies [11] measured liquid TTIP densities from 298 to 396 K and viscosities from 403 to 463 K. Nikitin et al. [12] determined the critical temperature and pressure of TTIP using a pulse-heating method. Bradley et al. [13] measured the boiling temperature of TTIP at low pressures (0.013 and 0.66 kPa). Lappert et al. [14] and Bradley and Hillyer [15] measured the heat of formation and the heat of combustion of TTIP.

It is well-known that at elevated temperatures, metal alkoxides can decompose chemically by splitting off the corresponding alcohol, which is 2-propanol in case of TTIP. Siefering and Griffin [16] investigated the decomposition of TTIP vapor by measuring the TiO_2 -growth rate for different temperatures and pressures. Bradley and coworkers [17,18] showed that for zirconium alkoxides, the hydrolysis to zirconium oxide and the corresponding alcohol is a chain reaction, which is catalyzed by glass surfaces. Ritala et al. [19] assumed a similar mechanism also for titanium alkoxides such as TTIP, which are chemically similar to zirconium alkoxides.

The most popular solvent for TTIP in the flame spray pyrolysis process is 2-propanol. However, the quite high vapor pressure of 2-propanol limits the range of the synthesis parameters towards the low pressure. In lab-scale investigations, the process pressure is a comfortable parameter to control the residence time and the flame properties. Thus, in this work, *p*-xylene was investigated as an alternative solvent with low vapor pressure.

To summarize: the decomposition mechanisms and some pure component properties of TTIP are known from literature studies. However, no data on thermophysical properties of solutions of TTIP are available, which hampers spray

flame process design and simulation. Hence, in the present work, a comprehensive experimental study on the VLE, specific density, viscosity, thermal conductivity, molar isobaric heat capacity, and self-diffusion coefficients of mixtures of TTIP and *p*-xylene was carried out. Correlations of the new experimental data are provided to facilitate the use of the results, e.g. in numerical simulations. In the present work, the reported uncertainties are standard uncertainties, which include statistical and method uncertainties. For the sake of brevity, we write “density” for “specific density” and “isobaric heat capacity” for “molar isobaric heat capacity”.

2. Experimental

2.1 Chemicals and sample preparation

TTIP and *p*-xylene were purchased from Sigma-Aldrich and analyzed by quantitative Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectroscopy in our laboratory. Results are presented in Table 1. Both chemicals were used without further purification. Due to the reaction of TTIP with air moisture, TTIP was handled in a dry nitrogen atmosphere in a glove-box. Samples were hermetically sealed in 40 mL glass vials. A laboratory balance (Mettler-Toledo AG204) with an accuracy of ± 0.0001 g according to the calibration protocol was used for the gravimetric sample preparation. The balance accuracy results in an uncertainty in the mole fraction of both components of ± 0.0005 mol mol $^{-1}$.

2.2 Measurements

2.2.1 Vapor-liquid equilibrium

The VLE measurements were performed using a recirculating glass still similar to the one described by Rafflenbeul and Hartmann [20]. A detailed description of the setup and its operation is given by Hasse [21]. The pressure is measured with a

pressure sensor (WIKA P-30) with an uncertainty of ± 0.4 kPa. The temperature is measured in the phase separation chamber with a Pt100 resistance thermometer that was calibrated in our laboratory against a standard certified by Physikalisch-Technische Bundesanstalt (PTB) Braunschweig. The uncertainty of the temperature measurement is ± 0.2 K. To test the apparatus, the boiling temperature of *p*-xylene was measured at pressures ranging from 20 to 80 kPa. The deviation between our data to the mean of the literature data in the observed boiling temperature is less than ± 0.2 K for all pressures, which is below the uncertainty specified above.

The mole fractions of TTIP and *p*-xylene in the coexisting phases were analyzed using quantitative ^1H -NMR spectroscopy. Analysis by gas chromatography was tested but not found feasible due to TTIP decomposition in the device. The ^1H -NMR experiments were carried out with a Bruker Ascend 400 MHz spectrometer, using 8 scans, a pulse width of 10° and a relaxation delay of 10 s. The accuracy of the NMR analysis was determined by analyzing gravimetrically-prepared mixtures of TTIP and *p*-xylene. From this analysis, the uncertainty in the mole fraction of both components is estimated to be better than ± 0.005 mol mol $^{-1}$.

During some of the VLE measurements, especially at temperatures above 420 K, the formation of small amounts of TiO_2 dust was observed visually in the circulating liquid. It results from the thermal decomposition of TTIP at high temperatures, together with a formation of 2-propanol [10,18,19]. If in the ^1H -NMR spectra any signal other than those of TTIP and *p*-xylene had an area greater than 1 % of the total area, the measurement was dismissed and is not reported in the present work. Hence, an uncertainty of ± 0.01 mol mol $^{-1}$ is obtained for the mole fractions of both

components in the liquid and gaseous phases. Furthermore, other method uncertainties might arise from this which cannot be quantified precisely.

2.2.2 *Density and viscosity*

Density and viscosity measurements were performed at 101.3 kPa with an instrument of Anton Paar (SVM 3000), which is a combination of a vibrating tube densimeter and a Stabinger viscosimeter. The temperature ranges from 293.15 to 373.15 K and the sample compositions cover the range from pure TTIP to pure *p*-xylene. The measurements of the density were conducted according to the ASTM method D4052, the uncertainty of the density is estimated to be $\pm 0.0005 \text{ g cm}^{-3}$. The measurements of the viscosity were conducted according to the ASTM method D7042, the relative uncertainty is estimated to be 3 %. After each set of measurements, the apparatus was cleaned twice with 2-propanol and toluene and flushed with dry air. The temperature was measured with a built-in thermometer for which the manufacturer reports an uncertainty of $\pm 0.05 \text{ K}$. The apparatus was calibrated with calibration standards provided by the manufacturer. For validation, the density and viscosity of pure *p*-xylene were measured and compared to literature data. The results are presented in the Supporting Information. Over the entire temperature range, the maximum deviation of our density data to the mean of the literature data is below 0.0004 g cm^{-3} , and the maximum relative deviation of our viscosity data to the mean of the literature data is below 3 %, which is within the uncertainties specified above for both properties.

2.2.3 *Thermal conductivity and isobaric heat capacity*

Thermal conductivity and isobaric heat capacity measurements were performed at 101.3 kPa with an instrument of flucon fluid control GmbH (LAMBDA), in which

the sensor and sample are thermostatted by a double jacket vessel. The temperatures were 293.15, 313.15 and 333.15 K and the sample compositions cover the range from pure TTIP to pure *p*-xylene. In the instrument, the thermal conductivity λ and the thermal diffusivity a are measured with the transient hot wire liquid thermal conductivity method according to ASTM method D7896. The isobaric heat capacity c_p is determined by the relationship

$$c_p = \frac{\lambda \cdot \bar{M}}{a \cdot \rho} \quad , \quad (1)$$

where ρ is the density of the liquid, which was determined as explained above, and $\bar{M}$ is the mean molar mass of the mixture. For each data point, the values for λ and c_p were averaged over at least 5 min. The uncertainty of the thermal conductivity measurement is estimated to be below $\pm 5.2 \text{ mW m}^{-1}\text{K}^{-1}$, and the relative uncertainty of the isobaric heat capacity measurement is estimated to be below 5 %. After each set of measurements, the apparatus was cleaned with 2-propanol and toluene and flushed with dry air. The temperature was measured with a built-in Pt100 resistance thermometer which was tested in our laboratory against a standard certified by PTB Braunschweig. The uncertainty of the temperature measurement is $\pm 0.2 \text{ K}$. The apparatus was calibrated to the thermal conductivity of toluene at 293.15 K. For validation, the thermal conductivity and isobaric heat capacity of pure *p*-xylene were measured and compared to literature data. The results are presented in the Supporting Information. Over the entire temperature range, the maximum deviation of our thermal conductivity data to the mean of the literature data is below $\pm 4 \text{ mW m}^{-1}\text{K}^{-1}$, and the maximum relative deviation of our isobaric heat capacity data to the mean of

the literature data is below 2 %, which is within the uncertainties specified above for both properties.

2.2.4 Self-Diffusion

¹H-NMR measurements of self-diffusion coefficients of TTIP and *p*-xylene were conducted at 101.3 kPa using a Bruker Ascend 400 MHz spectrometer as explained in more detail in the Supporting Information. The temperatures were 288.15, 298.15 and 308.15 K and the sample compositions cover the range from pure TTIP to pure *p*-xylene. In the spectrometer, the stimulated spin-echo technique with bipolar pulsed gradients as described by Stejskal and Tanner [22] is applied. The relative uncertainty of the self-diffusion coefficients is estimated to be 2 %. The spectrometer's temperature sensor was calibrated in our laboratory against a standard certified by PTB Braunschweig. The uncertainty of the temperature measurement is estimated to be below ± 0.2 K.

3. Modeling

3.1 Vapor-liquid equilibrium

The VLE is modeled with the extended Raoult's law,

$$p_i^S \cdot x_i \cdot \gamma_i = p \cdot y_i \quad , \quad (2)$$

where x_i and y_i are the mole fractions of component i in the liquid and gas phase, p_i^S is the vapor pressure of component i , γ_i is the liquid phase activity coefficient of component i and p is the pressure in the system. The pressure dependence of the chemical potential in the liquid phase is neglected and the vapor phase is treated as an ideal gas mixture. The vapor pressures p_i^S of the pure substances TTIP (1) and *p*-xylene (2) are modeled with a three parameter Antoine type equation

$$\ln(p_i^s / \text{kPa}) = A_i - \frac{B_i}{T / \text{K} + C_i} \quad , \quad (3)$$

where T is the temperature in K and A_i , B_i and C_i are adjustable parameters. The non-ideality of component i in the liquid phase is described with activity coefficients γ_i modeled by the NRTL equation,

$$\ln \gamma_i = x_j^2 \cdot \left[\tau_{ji} \cdot \left(\frac{G_{ji}}{x_i + x_j \cdot G_{ji}} \right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i \cdot G_{ij})^2} \right] \quad (4)$$

where

$$\ln G_{ij} = -\alpha_{ij} \cdot \tau_{ij} \quad . \quad (5)$$

The τ_{ij} 's and $\alpha_{ij} = \alpha_{ji}$ are adjustable parameters which were obtained from a fit to the measured VLE data.

3.2 Density, thermal conductivity and isobaric heat capacity

The density ρ is related to the molar volume v of a mixture by

$$v = \frac{\bar{M}}{\rho} \quad , \quad (6)$$

where $\bar{M}$ is the mean molar mass of the mixture. The molar volume of a mixture can be written as

$$v = x_1 v_1^{\text{pure}} + x_2 v_2^{\text{pure}} + v^{\text{E}} \quad , \quad (7)$$

where the v_i^{pure} are the pure component molar volumes and v^{E} is the molar excess volume. The temperature dependence of the pure component molar volumes is correlated by

$$v_i^{\text{pure}} / \text{m}^3 \text{mol}^{-1} = a_i + b_i \cdot (T / \text{K}) + c_i \cdot (T / \text{K})^2 \quad , \quad (8)$$

where, a_i , b_i and c_i are adjustable parameters. The molar excess volume is described using a Redlich-Kister correlation,

$$v^E / \text{m}^3 \text{mol}^{-1} = (E + F \cdot (T / \text{K})) \cdot x_1 x_2, \quad (9)$$

where E and F are adjustable parameters. Thermal conductivities λ (in units of $\text{mW m}^{-1} \text{K}^{-1}$) and molar isobaric heat capacities c_p (in units of $\text{J mol}^{-1} \text{K}^{-1}$) are correlated in the same way as the molar volume (in units of $\text{m}^3 \text{mol}^{-1}$) by means of Eq. (7) - (9).

3.3 Viscosity

Mixture viscosities η are described with the Jouyban-Acree correlation [23]

$$\begin{aligned} \ln \frac{\eta}{\text{mPa s}} = & x_1 \ln \left(\frac{\eta_1^{\text{pure}}}{\text{mPa s}} \right) + x_2 \ln \left(\frac{\eta_2^{\text{pure}}}{\text{mPa s}} \right) + E \left(\frac{x_1 x_2}{T / \text{K}} \right) \\ & + F \left(\frac{x_1 x_2 (x_1 - x_2)}{T / \text{K}} \right) + G \left(\frac{x_1 x_2 (x_1 - x_2)^2}{T / \text{K}} \right), \end{aligned} \quad (10)$$

where E , F and G are adjustable parameters. The temperature-dependent pure component viscosities η_i^{pure} are correlated by

$$\eta_i^{\text{pure}} = a_i \cdot \exp \left(\frac{b_i}{T / \text{K}} \right) + c_i, \quad (11)$$

where a_i , b_i and c_i are adjustable parameters.

3.4 Self-Diffusion

Self-diffusion coefficients D_i of both components in mixtures of TTIP and *p*-xylene are correlated separately for TTIP and *p*-xylene as

$$\begin{aligned} D_i / (10^{-9} \text{m}^2 \text{s}^{-1}) = & a_i + b_i \cdot (T / \text{K}) + (c_i + d_i \cdot (T / \text{K})) \cdot x_i \\ & + (e_i + f_i \cdot (T / \text{K})) \cdot x_i^2, \end{aligned} \quad (12)$$

where $a_i - f_i$ are adjustable parameters.

3.5 Fitting procedure

The adjustable parameters in the correlations introduced above were obtained by a least squares minimization using the MATLAB solver “lsqnonlin”. For the VLE, for all measured x_j^{exp} the objective function

$$\text{OF}_{\text{VLE}} = \sum_{j=1}^{N_p} \left(\frac{T_j^{\text{exp}} - T_j^{\text{cal}}}{T_j^{\text{exp}}} \right)^2 + \sum_{j=1}^{N_p} \left(\frac{y_j^{\text{exp}} - y_j^{\text{cal}}}{y_j^{\text{exp}}} \right)^2 \quad (13)$$

was minimized, where N_p is the number of experimental points. The superscripts “exp” and “cal” denote experimental and calculated results. The objective function for fitting the temperature dependence of the pure component molar volumes and the excess molar volume was

$$\text{OF}_v = \sum_{j=1}^{N_p} \left(\frac{v_j^{\text{exp}} - v_j^{\text{cal}}}{v_j^{\text{exp}}} \right)^2. \quad (14)$$

The viscosity, thermal conductivity, isobaric heat capacity and self-diffusion coefficients were fitted in the same way as the molar volume by means of Eq. (14).

4. Results and discussion

In the following section, results for the properties of mixtures of TTIP and *p*-xylene are shown as functions of the composition and the temperature. The experimental results are reported in Tables 2 - 7. The parameters of the correlations (cf. Eq. (2) – (12)) are given in Tables 8 - 12.

4.1 Vapor-liquid equilibrium

The experimental data of the VLE in the system TTIP + *p*-xylene are shown together with the NRTL model in Figure 1 for the lowest and highest considered total pressure (20 and 80 kPa).

[Figure 1 about here.]

Figure 1 shows a zeotropic behavior of the system. The model describes the experimental data fairly well. At high temperatures, some deviations are observed that may be related to the beginning decomposition of TTIP.

4.2 *Density*

The experimental data of the density of TTIP and *p*-xylene obtained in the present work are shown in Figure 2 together with the correlations.

[Figure 2 about here.]

The density of mixtures of TTIP and *p*-xylene increases with increasing amount of TTIP, and, not surprisingly, with decreasing temperature. The correlation describes the experimental data within the experimental uncertainty.

4.3 *Viscosity*

The experimental data of the viscosity of TTIP and *p*-xylene obtained in the present work are shown in Figure 3 together with the correlations.

[Figure 3 about here.]

The viscosity of mixtures of TTIP and *p*-xylene increases with increasing amount of TTIP, and, not surprisingly, with decreasing temperature. The correlation describes the experimental data well. At high concentrations of TTIP, where a steep increase of the viscosity is observed, some deviations are apparent, especially at low temperatures. These deviations were, however, not deemed to be so important as to resort to a more complex correlation, which would involve the risk of overfitting.

4.4 *Thermal conductivity*

The experimental data of the thermal conductivity of TTIP and *p*-xylene obtained in the present work are shown in Figure 4 together with the correlations.

[Figure 4 about here.]

The thermal conductivities of pure TTIP and pure *p*-xylene have similar values in the studied temperature range. In mixtures of TTIP and *p*-xylene, no significant excess contribution to the thermal conductivity is observed. Therefore, the corresponding Redlich-Kister parameter for the thermal conductivity was set to zero, cf. Table 11. The correlation describes the experimental data within the experimental uncertainty.

4.5 *Isobaric heat capacity*

The experimental data of the isobaric heat capacity of TTIP and *p*-xylene obtained in the present work are shown in Figure 5 together with the correlations.

[Figure 5 about here.]

For all temperatures, the isobaric heat capacity decreases with increasing amount of TTIP. As expected, the isobaric heat capacity increases with increasing temperature. The correlation describes the experimental data within the experimental uncertainty.

4.6 *Self-Diffusion*

The experimental data of the self-diffusion coefficients of TTIP and *p*-xylene obtained in the present work are shown in Figure 6 together with the correlations.

[Figure 6 about here.]

The self-diffusion coefficients of both TTIP and *p*-xylene decrease with increasing amount of TTIP and decreasing temperature. The self-diffusion coefficient of *p*-xylene is always higher than that of TTIP, which is not astonishing as *p*-xylene is the smaller molecule. Furthermore, the trends in the self-diffusion coefficient data match the expectations: the self-diffusion coefficient of both species is high where the

viscosity and the density are low and vice versa. The correlation describes the experimental data within the experimental uncertainty.

5. Conclusions

In the present work, thermophysical properties of mixtures of Titanium(IV) Isopropoxide (TTIP) and *p*-xylene, which are of interest for the design of spray flame synthesis process of TiO₂ nanoparticles, were studied experimentally. The studied properties are: the vapor-liquid equilibrium, specific densities, viscosities, thermal conductivities, molar isobaric heat capacities, and self-diffusion coefficients. No information on these properties was previously available. Empirical correlations for all properties are provided. They describe the experimental data within their uncertainty. The data and correlations presented here provide a sound basis for the design and optimization of spray flame processes for the production of titanium nanoparticles.

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7. References

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Table 1: Chemical specification.

	CAS reg. no.	supplier	purity	analysis method
TTIP	546-68-9	Sigma Aldrich	$\geq 0,99$ mol/mol	^1H -NMR spectroscopy
<i>p</i> -xylene	106-42-3	Sigma Aldrich	$\geq 0,99$ mol/mol	^1H -NMR spectroscopy

Table 2: Results of the VLE measurements; pressure p , temperature T , mole fractions in the liquid and vapor phase (x_{TTIP} and y_{TTIP}). Uncertainties are $u(p) = 0.4$ kPa, $u(T) = 0.2$ K, and $u(x_{\text{TTIP}}) = u(y_{\text{TTIP}}) = 0.01$ mol mol $^{-1}$.

p kPa	T K	x_{TTIP} mol mol $^{-1}$	y_{TTIP} mol mol $^{-1}$	p kPa	T K	x_{TTIP} mol mol $^{-1}$	y_{TTIP} mol mol $^{-1}$
20	364.6	0.1412	0.0061	40	384.3	0.1437	0.0108
	367.4	0.2501	0.0199		391.6	0.2314	0.0231
	369.4	0.2739	0.0148		394.7	0.2627	0.0298
	377.6	0.3581	0.0329		396.1	0.2948	0.0345
	393.3	0.5532	0.1025		398.1	0.3205	0.0398
	408.7	0.7300	0.2425		437.5	0.6746	0.3676
	401.1	0.7153	0.1639		455.9	0.9180	0.7432
	414.1	0.8160	0.3123	50	396.1	0.1734	0.0151
30	420.8	0.8815	0.4204		392.0	0.1348	0.0072
	374.3	0.1060	0.0153		403.7	0.3284	0.0327
	377.5	0.1335	0.0093	60	407.9	0.3532	0.0514
	381.8	0.2490	0.0181		397.3	0.1141	0.0113
	387.8	0.2991	0.0303		404.9	0.1932	0.0525
	409.0	0.6719	0.1374		410.6	0.3349	0.0365
	417.0	0.7239	0.2194	70	414.8	0.3664	0.0570
	429.8	0.8731	0.4406		434.4	0.6772	0.1938
40	434.4	0.8946	0.5326		410.7	0.1875	0.0229
	380.2	0.0168	0.0000	80	416.6	0.3456	0.0480
	380.6	0.0233	0.0017		421.4	0.3808	0.0674
	381.0	0.0376	0.0043		407.8	0.1279	0.0093
	381.3	0.0509	0.0045		413.1	0.1824	0.0182
	381.6	0.0630	0.0061		424.0	0.3561	0.0575
	382.5	0.0907	0.0063		421.6	0.3356	0.0468
	383.4	0.1112	0.0085		440.8	0.5347	0.1695

Table 3: Results of the density measurements; density ρ , liquid mole fraction x_{TIP} and temperature T . The uncertainties are $u(\rho) = 0.0005 \text{ g cm}^{-3}$, $u(x_{\text{TIP}}) = 0.0005 \text{ mol mol}^{-1}$ and $u(T) = 0.05 \text{ K}$.

x_{TIP} mol mol ⁻¹	$\rho / \text{g cm}^{-3}$								
	$T=293.15 \text{ K}$	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K
0.0000	0.8609	0.8522	0.8434	0.8347	0.8259	0.8169	0.8080	0.7990	0.7896
0.0401	0.8695	0.8605	0.8515	0.8424	0.8334	0.8243	0.8152	0.8060	0.7967
0.0871	0.8781	0.8687	0.8594	0.8502	0.8410	0.8318	0.8225	0.8131	0.8037
0.1382	0.8877	0.8778	0.8680	0.8582	0.8487	0.8393	0.8298	0.8203	0.8109
0.1994	0.8979	0.8874	0.8770	0.8667	0.8567	0.8469	0.8372	0.8276	0.8179
0.2719	0.9062	0.8947	0.8840	0.8737	0.8635	0.8536	0.8439	0.8342	0.8244
0.3593	0.9170	0.9044	0.8929	0.8820	0.8714	0.8612	0.8513	0.8414	0.8315
0.4654	0.9289	0.9152	0.9027	0.8911	0.8800	0.8693	0.8590	0.8489	0.8390
0.5987	0.9413	0.9261	0.9125	0.9001	0.8885	0.8774	0.8667	0.8564	0.8462
0.7700	0.9531	0.9362	0.9214	0.9081	0.8959	0.8845	0.8736	0.8631	0.8529
1.0000	0.9660	0.9473	0.9298	0.9154	0.9027	0.8912	0.8802	0.8696	0.8593

Table 4: Results of the viscosity measurements; viscosity η , liquid mole fraction x_{TIP} and temperature T . The uncertainties are $u_r(\eta) = 3 \%$, $u(x_{\text{TIP}}) = 0.0005 \text{ mol mol}^{-1}$ and $u(T) = 0.05 \text{ K}$.

x_{TIP} mol mol ⁻¹	$\eta / \text{mPa s}$								
	$T=293.15 \text{ K}$	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K
0.0000	0.65894	0.57716	0.51173	0.45713	0.41281	0.37636	0.34670	0.32305	0.29867
0.0401	0.67099	0.58811	0.52264	0.46554	0.42071	0.38363	0.35188	0.32547	0.30300
0.0871	0.70979	0.62152	0.54936	0.48958	0.44153	0.40106	0.36193	0.33864	0.31670
0.1382	0.76517	0.66486	0.58127	0.51618	0.46447	0.42257	0.38709	0.35691	0.33100
0.1994	0.83728	0.71527	0.62377	0.55006	0.49267	0.44629	0.40839	0.37220	0.34761
0.2719	0.91425	0.76951	0.66414	0.58489	0.52080	0.47181	0.43110	0.39548	0.36616
0.3593	1.04190	0.85502	0.72576	0.63262	0.55971	0.50446	0.45762	0.41884	0.38618
0.4654	1.23460	0.97237	0.80578	0.69216	0.60745	0.54333	0.49133	0.44818	0.41225
0.5987	1.53010	1.13740	0.91112	0.76640	0.66452	0.58825	0.52869	0.48225	0.44197
0.7700	2.05280	1.39800	1.06340	0.87098	0.74421	0.65185	0.58164	0.52521	0.47976
1.0000	3.14432	1.84518	1.27912	1.00344	0.84298	0.73577	0.65682	0.59470	0.54454

Table 5: Results of the thermal conductivity measurements; thermal conductivity λ , liquid mole fraction x_{TIP} and temperature T . The uncertainties are $u(x_{\text{TIP}}) = 0.0005 \text{ mol mol}^{-1}$, $u(T) = 0.2 \text{ K}$, $u(\lambda)$ is given for each point in the table.

x_{TIP} mol mol ⁻¹	$\lambda / \text{mW m}^{-1} \text{ K}^{-1}$		
	$T = 293.15 \text{ K}$	313.15 K	333.15 K
0.0000	126.81 $\pm$ 3.15	122.22 $\pm$ 5.11	117.05 $\pm$ 3.08
0.0401	126.85 $\pm$ 1.71	120.59 $\pm$ 1.52	115.68 $\pm$ 1.43
0.0871	127.54 $\pm$ 1.47	122.46 $\pm$ 1.72	114.64 $\pm$ 2.55
0.1382	127.43 $\pm$ 1.40	122.24 $\pm$ 1.38	116.21 $\pm$ 1.24
0.1994	126.71 $\pm$ 1.42	123.38 $\pm$ 1.30	116.31 $\pm$ 1.41
0.2718	127.89 $\pm$ 1.48	123.79 $\pm$ 1.46	116.48 $\pm$ 1.78
0.3593	127.49 $\pm$ 1.39	124.26 $\pm$ 1.41	117.12 $\pm$ 1.34
0.4654	131.27 $\pm$ 1.51	123.28 $\pm$ 1.51	116.79 $\pm$ 1.52
0.5988	130.34 $\pm$ 1.45	122.55 $\pm$ 1.34	116.21 $\pm$ 2.75
0.7700	132.18 $\pm$ 1.40	123.72 $\pm$ 1.47	116.76 $\pm$ 1.58
1.0000	131.98 $\pm$ 1.53	125.39 $\pm$ 1.43	117.06 $\pm$ 1.62

Table 6: Results of the isobaric heat capacity measurements; isobaric heat capacity c_p , liquid mole fraction x_{TIP} and temperature T . The uncertainties are $u_r(c_p) = 5 \%$, $u(x_{\text{TIP}}) = 0.0005 \text{ mol mol}^{-1}$ and $u(T) = 0.2 \text{ K}$.

x_{TIP} mol mol ⁻¹	$c_p / \text{J mol}^{-1} \text{ K}^{-1}$		
	$T = 293.15 \text{ K}$	313.15 K	333.15 K
0.0000	182.6	186.9	191.1
0.0401	193.8	196.0	200.6
0.0871	206.9	211.7	215.4
0.1382	219.7	224.9	227.6
0.1994	235.2	242.3	243.7
0.2718	255.0	262.8	264.3
0.3593	277.3	287.5	289.2
0.4654	313.8	313.8	319.5
0.5988	344.7	346.8	353.2
0.7700	396.5	396.5	401.4
1.0000	457.6	466.1	466.1

Table 7: Results of the self-diffusion coefficient measurements; self-diffusion coefficient D_i of component i , liquid mole fraction x_{TTIP} and temperature T . The uncertainties are $u(D_i) = 5.5 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $u(x_{\text{TTIP}}) = 0.0005 \text{ mol mol}^{-1}$ and $u(T) = 0.2 \text{ K}$.

x_{TTIP} mol mol ⁻¹	$D_i / 10^{-9} \text{ m}^2 \text{ s}^{-1}$					
	$T = 288.15 \text{ K}$		298.15 K		308.15 K	
	$i = p\text{-xylene}$	TTIP	$p\text{-xylene}$	TTIP	$p\text{-xylene}$	TTIP
0.0108	2.0789	1.1880	2.3993	1.5613	2.7528	1.6825
0.0708	1.9564	1.1179	2.2523	1.3160	2.5750	1.5246
0.1578	1.8357	0.9852	2.0898	1.1279	2.4274	1.3365
0.2876	1.6315	0.8189	1.8922	0.9634	2.2141	1.1626
0.5607	1.3377	0.5945	1.6155	0.7594	1.9441	0.9509
0.9851	0.8475	0.2936	1.1102	0.4659	1.5032	0.6470

Table 8: Antoine parameters for the vapor pressures of pure TTIP and p -xylene obtained from a fit to the referenced experimental data from the literature, cf. Eq. (3).

	A	B	C	Ref.
TTIP	12.9502	2998.2	-139.586	[24,25]
p -xylene	14.0775	3344.9	-57.910	[26]

Table 9: NRTL parameters for the system TTIP (1) + p -xylene (2) obtained from a fit to experimental data from the present work, cf. Eqs. (2) - (5).

Non-randomness parameter	$\alpha_{12} = \alpha_{21}$	0.49
NRTL fit parameters	τ_{12}	-1.1078
	τ_{21}	0.8699

Table 10: Parameters of the correlations for the pure component properties of TTIP and *p*-xylene.

Property	Eq.	Component	<i>a</i>	<i>b</i>	<i>c</i>
Molar volume $v / \text{m}^3 \text{mol}^{-1}$	(8)	TTIP	$-1.1177 \cdot 10^{-6}$	$1.4478 \cdot 10^{-6}$	$-1.4989 \cdot 10^{-9}$
		<i>p</i> -xylene	$8.2479 \cdot 10^{-5}$	$1.3870 \cdot 10^{-7}$	0
Viscosity $\eta / \text{mPa s}$	(11)	TTIP	$1.0491 \cdot 10^{-8}$	$5.6646 \cdot 10^3$	$5.3571 \cdot 10^{-1}$
		<i>p</i> -xylene	$2.9350 \cdot 10^{-3}$	$1.5259 \cdot 10^3$	$1.0526 \cdot 10^{-1}$
Thermal conductivity $\lambda / \text{mW m}^{-1} \text{K}^{-1}$	(8)	TTIP	$2.4174 \cdot 10^2$	$-3.7335 \cdot 10^{-1}$	0
		<i>p</i> -xylene	$1.9823 \cdot 10^2$	$-2.4331 \cdot 10^{-1}$	0
Isobaric heat capacity $c_p / \text{J mol}^{-1} \text{K}^{-1}$	(8)	TTIP	$3.9646 \cdot 10^2$	$2.1337 \cdot 10^{-1}$	0
		<i>p</i> -xylene	$1.2443 \cdot 10^2$	$2.0026 \cdot 10^{-1}$	0

Table 11: Parameters of the Redlich-Kister correlation for molar volume, thermal conductivity and isobaric heat capacity (cf. Eq. (9)) and parameters of the Jouyban-Acree correlation for viscosity (cf. Eq. (10)).

	Eq.	<i>E</i>	<i>F</i>	<i>G</i>
Molar volume $v / \text{m}^3 \text{mol}^{-1}$	(9)	$1.7034 \cdot 10^{-5}$	$-5.3617 \cdot 10^{-8}$	-
Viscosity $\eta / \text{mPa s}$	(10)	$-2.7876 \cdot 10^1$	$-2.6167 \cdot 10^1$	$-1.1670 \cdot 10^2$
Thermal conductivity $\lambda / \text{mW m}^{-1} \text{K}^{-1}$	(9)	0	0	-
Isobaric heat capacity $c_p / \text{J mol}^{-1} \text{K}^{-1}$	(9)	$-9.1239 \cdot 10^0$	0	-

Table 12: Parameters of the correlations for the self-diffusion coefficients, cf. Eq. (12).

	a	b	c	d	e	f
TTIP	$-5.4126 \cdot 10^0$	$2.2988 \cdot 10^{-2}$	$4.9976 \cdot 10^0$	$-2.2444 \cdot 10^{-2}$	$-4.3365 \cdot 10^0$	$1.6975 \cdot 10^{-2}$
<i>p</i> -xylene	$-8.5659 \cdot 10^0$	$3.2589 \cdot 10^{-2}$	$4.8451 \cdot 10^0$	$-1.3521 \cdot 10^{-2}$	$-3.5545 \cdot 10^0$	$1.3354 \cdot 10^{-2}$

Figure 1: VLE of TTIP + *p*-xylene. Symbols are experimental results for the pressures ($\square$) 20 kPa and ($\circ$) 80 kPa. Lines show the NRTL model, cf. Eqs. (2) - (5), with parameters from Tables 8 and 9.

Figure 2: Densities ρ of mixtures of TTIP and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are always within symbol size. Lines are empirical correlations, cf. Eqs. (7) - (9), with parameters from Tables 10 and 11.

Figure 3: Viscosities η of mixtures of TTIP and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are always within symbol size. Lines are empirical correlations, cf. Eqs. (10) - (11), with parameters from Tables 10 and 11.

Figure 4: Thermal conductivities λ of mixtures of TTIP and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars are standard deviations of 10 subsequent measurements. Lines are empirical correlations, cf. Eqs. (7) - (9), with parameters from Tables 10 and 11.

Figure 5: Isobaric heat capacity c_p of mixtures of TTIP and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are always within symbol size. Lines are empirical correlations, cf. Eqs. (7) - (9), with parameters from Tables 10 and 11.

Figure 6: Self-diffusion coefficients D of TTIP and *p*-xylene in mixtures of the substances at 101.3 kPa and different temperatures. Symbols are experimental results for ($\square$) TTIP and (Δ) *p*-xylene. Experimental uncertainties are always within symbol size. Lines are empirical correlations, cf. Eq. (12), with parameters from Table 12.