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Fluid Properties and Droplet Evaporation Modeling for Spray Flame Synthesis

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Babette Kunstmann

Abstract

Spray flame synthesis is a versatile process for producing nanoparticles. In that process, a mixture of a combustible solvent with a metal-containing substance, the so-called precursor solution, is sprayed through a nozzle. The droplets are then ignited by contact with a pilot flame, eventually resulting in the formation of metal oxide nanoparticles. Thermophysical property data are essential for improving the understanding of the process and its rational design, but are unavailable for many precursor solutions. In the present work, fluid properties of mixtures of 2-ethylhexanoic acid (EHA) with ethanol or *p*-xylene, which are common solvents for precursor solutions, are studied. Moreover, fluid properties of mixtures of tin(II) 2-ethylhexanoate and *p*-xylene, which are e.g. used for the spray flame synthesis of gas sensor materials, are investigated. For these mixtures, the investigated properties include the density, viscosity, thermal conductivity, isobaric heat capacity, and self-diffusion coefficients of both components at temperatures between 293.15 and 353.15 K. Furthermore, isobaric vapor-liquid equilibria of mixtures of EHA with ethanol or *p*-xylene are measured at pressures below atmospheric pressure. Liquid-liquid equilibria in mixtures of EHA, ethanol, and water are measured at temperatures between 283 and 333 K. Correlations are established for all properties and provide a basis for process analysis and optimization e.g. by process simulations. In the spray flame process, micro-explosions of the evaporating droplets are believed to be key for achieving a homogeneous product quality, but their causes are under debate in the literature. A possible explanation for these micro-explosions is superheating inside the droplet, which can occur if heat conduction inside the droplet is faster than diffusive mass transport, i.e., for high Lewis numbers. For all studied systems, the Lewis numbers are high, indicating that superheating may occur inside the evaporating droplets. To study this in more detail, a one-dimensional evaporating droplet model that considers both the energy transport and the mass transport inside the droplet and the corresponding convective boundary conditions is developed and implemented. Simulations of the evaporation of droplets of titanium(IV) isopropoxide and *p*-xylene are carried out. The simulation results show that superheating sets in inside the droplet. Hence, after reaching a certain threshold, a sudden evaporation will occur inside the droplet – and cause the micro-explosion. This behavior is to be expected in all systems with high Lewis numbers.

Kurzfassung

Die Sprayflammsynthese ist eine vielseitige Herstellungsmethode für Nanopartikel. Dabei wird eine Mischung aus einem brennbaren Lösungsmittel und einer metallhaltigen Substanz, die so genannte Präkursorlösung, durch eine Düse versprüht. Die Tröpfchen entzünden sich an einer Pilotflamme und schließlich entstehen Metalloxid-Nanopartikel. Für ein besseres Prozessverständnis und eine gezielte Prozessauslegung sind Daten zu thermophysikalischen Eigenschaften unerlässlich, die jedoch für viele Präkursorlösungen nicht verfügbar sind. In der vorliegenden Arbeit werden die Stoffeigenschaften von Mischungen von 2-Ethylhexansäure (EHA) mit Ethanol oder *p*-Xylol untersucht, die häufig als Lösungsmittel für Präkursorlösungen verwendet werden. Darüber hinaus werden Stoffeigenschaften von Mischungen von Zinn(II)-2-ethylhexanoat mit *p*-Xylol vermessen, die beispielsweise zur Herstellung von Gassensormaterialien eingesetzt werden. Die untersuchten Stoffeigenschaften umfassen die Dichte, Viskosität, Wärmeleitfähigkeit, isobare Wärmekapazität und die Selbstdiffusionskoeffizienten beider Komponenten bei Temperaturen zwischen 293.15 und 353.15 K. Zudem werden isobare Dampf-Flüssigkeits Gleichgewichte von Mischungen von EHA mit Ethanol oder *p*-Xylol bei Unterdruck vermessen. Flüssig-flüssig Gleichgewichte von Mischungen aus EHA, Ethanol und Wasser werden bei Temperaturen zwischen 283 und 333 K untersucht. Für alle Eigenschaften werden Korrelationen entwickelt, die die Grundlage für die Analyse und Optimierung des Prozesses, z.B. mittels Prozesssimulationen, bilden. In der Sprayflamme auftretende Mikroexplosionen gelten als Schlüssel zu einer homogenen Produktqualität, ihre Ursachen werden jedoch in der Literatur kontrovers diskutiert. Eine wahrscheinliche Ursache ist eine Überhitzung im Tröpfcheninneren, die auftreten kann, falls dort die Wärmeleitung schneller als der diffusive Stofftransport ist, d.h. bei hohen Lewis-Zahlen. Die Lewis-Zahlen der untersuchten Stoffsysteme weisen hohe Werte auf. Um den Mechanismus genauer zu untersuchen, wird ein Modell entwickelt, das sowohl den Energie- und Massentransport im Tröpfchen als auch die entsprechenden konvektiven Randbedingungen berücksichtigt. Mit diesem Modell werden Simulationen zur Verdampfung von Tröpfchen aus Tetraisopropylorthotitanat und *p*-Xylol durchgeführt. Die Ergebnisse zeigen, dass im Tröpfcheninneren Überhitzungen auftreten, die ab einem bestimmten Schwellenwert zu einer schlagartigen Verdampfung und damit zu einer Mikroexplosion führen können. Dies ist für alle Stoffsysteme mit hohen Lewis-Zahlen zu erwarten.

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List of Symbols

Latin symbols

a	Thermal diffusivity
A_i	Parameter of the Antoine equation
a_{i,D_i}	Parameter for the self-diffusion coefficient of component i
$a_{i,z}$	Parameter for the correlation of property z of component i
a_{ij}	Temperature dependence parameter of the NRTL interaction parameter
B_i	Parameter of the Antoine equation
B_M	Spalding mass transfer number
B_T	Spalding heat transfer number
b_{i,D_i}	Parameter for the self-diffusion coefficient of component i
$b_{i,z}$	Parameter for the correlation of property z of component i
b_{ij}	Temperature dependence parameter of the NRTL interaction parameter
C_i	Parameter of the Antoine equation
c_{i,D_i}	Parameter for the self-diffusion coefficient of component i
$c_{i,z}$	Parameter for the correlation of property z of component i
c_p	Isobaric heat capacity
D	Fickian diffusion coefficient
d	Droplet diameter
$\mathcal{D}$	Maxwell-Stefan diffusion coefficient
D_i	Self-diffusion coefficient of component i
d_{i,D_i}	Parameter for the self-diffusion coefficient of component i
e_{i,D_i}	Parameter for the self-diffusion coefficient of component i
E_z	Parameter for the correlation of the excess of property z
f_{i,D_i}	Parameter for the self-diffusion coefficient of component i
F_z	Parameter for the correlation of the excess of property z
g	Field gradient strength
G_{ij}	NRTL parameter
G_z	Parameter for the correlation of the excess of property z
Δh^v	Enthalpy of vaporization
I	Signal intensity

k	Coverage factor for the combined expanded uncertainty
Le	Lewis number
m	Mass
M	Molar mass
N	Number of components
N_{exp}	Number of experimental data points
Nu	Nusselt number
p	Pressure
p_i^s	Pure component vapor pressure
Pr	Prandtl number
$\dot{Q}$	Heat flow
r	Radial coordinate
R	Droplet radius
Re	Reynolds number
S	Superheating index
Sc	Schmidt number
Sh	Sherwood number
T	Temperature
t	Time
u	Uncertainty
U	Combined expanded uncertainty
v	Molar volume
x	Mole fraction (liquid phase)
y	Mole fraction (gas phase)
z	Exemplary property

Superscripts and subscripts

exp	Experimental
calc	Calculated
rel	Relative
0	Initial
E	Excess property
i, j	Component indices
l	Summation index
(m)	Specific
pure	Pure component property
'	EHA-rich liquid phase

"	Water-rich liquid phase
∞	At infinite dilution
∞	Ambient (in the droplet evaporation model)
*	At threshold of superheating index

Greek symbols

α	Non-randomness parameter of NRTL model
γ_i	Activity coefficient of component i
Γ	Thermodynamic factor
δ	Duration of application of field gradient
Δ	Diffusion time
ε_i	Evaporation rate of component i
ζ	Correction constant for bipolar gradients
η	Viscosity
λ	Thermal conductivity
ρ	Density
ϱ	Gyromagnetic ratio
τ_{ij}	NRTL interaction parameter

Abbreviations

EEH	Ethyl 2-ethylhexanoate
EHA	2-Ethylhexanoic acid
LLE	Liquid-liquid equilibrium
NMR	Nuclear magnetic resonance
NRTL	Non-random two-liquid model
OF	Objective function
PTB	Physikalisch-Technische Bundesanstalt Braunschweig
SnEHA	Tin(II) 2-ethylhexanoate
TTIP	Titanium(IV) tetraisopropoxide
VLE	Vapor-liquid equilibrium

1 Introduction

Spray flame synthesis is a versatile aerosol process for the production of functional nanomaterials [1, 2] for applications in several fields, including gas sensors [3–5], energy [6–8], biomedicine [9, 10], and catalysis [11–13]. In this process, a metal salt or organometallic compound is dissolved in a flammable organic solvent. This so-called precursor solution is sprayed through a nozzle as a fine mist into a pilot flame. As a result, the precursor solution evaporates from the spray droplets and combusts. The formation of nanoparticles occurs through the interaction of various physical mechanisms of particle formation and particle growth. [1, 14–16] Overall, the properties of the product particles strongly depend on the evaporation and disintegration process of the precursor solution droplets. [1, 17] Depending on the properties of the precursor solution and the conditions in the spray flame along the droplet trajectory, nanoparticle formation occurs predominantly in the gas phase (gas-to-particle mechanism) or in the liquid phase (droplet-to-particle mechanism). From these two mechanisms, the gas-to-particle mechanism is the desired one, since it typically leads to homogeneous, high quality nanomaterials. [18, 19]

The gas-to-particle mechanism typically occurs when using precursor solutions such as organometallic compounds dissolved in xylene. [18] Therefore, the use of mixtures of, for example, tin(II) 2-ethylhexanoate (SnEHA) with *p*-xylene in the spray flame process, yields fine and homogeneous nanoparticles for specialized high-value applications. [3, 20, 21] However, due to the relatively high cost of such organometallic compounds, the use of cheaper precursors like metal nitrates dissolved in alcohols is becoming a focal point of research in the field of spray flame synthesis, especially with regard to the scale-up of the process. [22–24] However, without the addition of other components, such as 2-ethylhexanoic acid (EHA), to these mixtures of nitrates and alcohols, the product tends to consist of heterogeneous and large particles formed by the droplet-to-particle mechanism. [22] The positive effect of the addition of EHA on product quality is usually attributed to the promotion of micro-explosions due to internal superheating of the droplets. [22, 25, 26] These micro-explosions are considered to be key to high product quality with fine and homogeneous nanoparticles. [13, 25, 27]

Micro-explosions have been observed in studies of fuel blend droplet evaporation for a long time [28–32]. In this field, the occurrence of the micro-explosions of multicomponent

fuel droplets is usually attributed to a superheating inside the droplet, which gives rise to the explosion when vaporization sets in. This occurs only for mixtures and only when the heat conduction is faster than the mass diffusion. Then, the temperature inside the droplet in a hot atmosphere rises faster than the droplet interior is depleted from the low-boiling component that evaporates preferentially. Therefore, the droplet interior can become superheated and, eventually, homogeneous or heterogeneous vapor nucleation can occur. [28–32] The Lewis number Le is used as a measure for the ratio between heat conduction and mass diffusion rates. It is defined as:

$$Le = \frac{a}{D}, \quad (1)$$

where a is the liquid thermal diffusivity and D is the diffusion coefficient in the liquid phase. The thermal diffusivity a can be calculated from the thermal conductivity λ , the density ρ , and the isobaric heat capacity c_p :

$$a = \frac{\lambda}{\rho c_p} \quad (2)$$

High Lewis numbers indicate slow diffusive mass transport compared to fast heat conduction and, thus, a higher probability for droplet superheating and micro-explosion [28].

In order to deepen the fundamental understanding of the spray flame process, including complex phenomena such as micro-explosions, and to ultimately enable a targeted process design, data on the thermophysical properties of the precursor solutions are required. Thermophysical properties, and in particular thermodynamic models for them, are especially needed for carrying out simulations of the spray flame process. However, the necessary data are not available in the literature for most of the mixtures typically used in spray flame synthesis.

Therefore, this work studies the thermophysical properties of the commonly used solvent mixtures of EHA with ethanol (Chapter 4) or with *p*-xylene (Chapter 5), and mixtures of SnEHA with *p*-xylene (Chapter 6), which can be used for the production of gas sensing materials. The density, the viscosity, the thermal conductivity, the isobaric heat capacity, as well as the self-diffusion coefficients of both components in each of these mixtures were investigated over the entire concentration range at atmospheric pressure ($p = 101.3$ kPa) and temperatures between 293.15 and 353.15 K. All properties were modeled with empirical correlations, such as Redlich-Kister-type polynomials for excess properties and a Jouyban-Acree correlation for the mixture viscosities, to enable the convenient use of the results, for example, in simulations of the spray flame synthesis process. Additionally, isobaric vapor-liquid equilibria (VLE) of mixtures of EHA and ethanol were measured at pressures between 20 and 80 kPa. Isobaric VLE of mixtures

of EHA and *p*-xylene were measured at pressures of 10 and 20 kPa. For both systems, thermodynamic models for the VLE were developed. The results for the thermophysical properties allow further studies, including the calculation of the Lewis numbers of the investigated mixtures.

Moreover, liquid-liquid equilibria (LLE) in mixtures of (EHA + ethanol + water), including the binary subsystem (EHA + water), were investigated at atmospheric pressure and temperatures between 283 and 333 K in Chapter 7. Using the LLE data from Chapter 7 and VLE data from the literature and Chapter 4, two versions of a thermodynamic model for the ternary system were developed. One version represents the LLE data well but is less accurate for the VLE in the binary subsystem (ethanol + water), for the other version it is vice-versa. Using the model, residue curves were calculated in order to make an estimate if liquid-liquid demixing might occur in an evaporating spray flame droplet.

Finally, Chapter 8 investigates whether superheating is a possible cause of the micro-explosions in spray flame synthesis by simulating an evaporating droplet consisting of the precursor titanium(IV) isopropoxide (TTIP) dissolved in *p*-xylene. Data from single droplet combustion experiments are available, which confirm the occurrence of micro-explosions in this system. [33] The droplet is described by a one-dimensional model in spherical coordinates, accounting for both diffusion and heat conduction in the droplet, alongside with the corresponding convective boundary conditions. From the concentration and temperature profiles, information on the superheating is obtained. The degree of superheating that is needed to induce evaporation is hard to estimate for the extremely high rates of the temperature and concentration changes in the droplets in spray flame synthesis. Furthermore, not only homogeneous but also heterogeneous nucleation might occur [27]. However, the occurrence of some degree of internal superheating of the droplet makes micro-explosions generally possible and would thus provide an explanation for their incidence.

2 Experimental

2.1 Chemicals and Sample Preparation

The molar masses, CAS registry numbers, suppliers, and purities of the chemicals used in this work are listed in Table 1. The samples were prepared gravimetrically using a Mettler-Toledo AG204 laboratory balance (specified standard uncertainty $u(m) = 0.0001$ g of the mass m) for sample masses smaller than 50 g and a Mettler-Toledo PR2003 Comparator laboratory balance (specified standard uncertainty $u(m) = 0.001$ g) for larger samples. From error propagation, the uncertainty of the mole fraction x due to the uncertainty of the mass is estimated to be $U(x) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$). 1,4-Dioxane was used as an internal standard for gas chromatography. Water was deionized and purified with a Milli-Q Reference A+ purification system by Merck Millipore.

All chemicals except for SnEHA were used without further purification. The as-purchased SnEHA was found to contain impurities which are most likely EHA [34, 35], originating either from the production process [35] or the hydrolysis of SnEHA [34]. Therefore, SnEHA was purified in a rotary evaporator (Laborota 4011-digital, Heidolph, with Laboratory Vacuum System LVS 210 Tp, Ilmvac) at 2 mbar and 180 °C for approximately 2 h. The purity of SnEHA before and after purification was evaluated by ^1H nuclear magnetic resonance (NMR) spectroscopy. Assuming that EHA is the only remaining impurity, by this treatment, the SnEHA purity could be increased from 0.67 to 0.98 mol mol $^{-1}$. Details on these ^1H NMR measurements are reported in the Appendix.

Table 1: Chemical specifications.

Chemical	Molar mass / kg mol $^{-1}$	CAS reg. no.	Supplier	Mole fraction purity
2-ethylhexanoic acid (EHA)	0.14421	149-57-5	Sigma-Aldrich	0.998 ^a
ethanol (EtOH)	0.04607	64-17-5	Supelco	$\geq 0.999^a$
<i>p</i> -xylene (Xyl)	0.10617	106-42-3	Thermo Fisher Scientific	0.997 ^a
tin(II) 2-ethylhexanoate (SnEHA)	0.40512	301-10-0	Sigma-Aldrich	0.98 ^b
1,4-dioxane	0.08811	123-91-1	Sigma-Aldrich	0.9993 ^a

^a As specified by the supplier.

^b After purification by evaporation, determined by ^1H NMR spectroscopy.

2.2 Measurements

All measurements except for the VLE measurements were conducted at atmospheric pressure ($p = 101.3$ kPa). The ambient pressure was monitored with a mercury barometer. The highest day-to-day fluctuations were approximately 3 kPa. Therefore, the uncertainty of the pressure is estimated to be $u(p) = 3$ kPa.

All experimental methods were the same as in the works of Keller et al. [36, 37, 38, 39]. Only the sample composition analysis for the VLE measurements was methodically different as explained in Section 2.2.4. In Appendix A, a comparison of the experimental results for the pure component properties of EHA and ethanol from Chapter 4 and the literature is shown. As in Ref. 38, good agreement was obtained in all cases. Additional data for the self-diffusion coefficient of pure EHA as a function of temperature at temperatures between 298.15 and 353.15 K, for which no data for comparison are available in the literature, are also given in Appendix A. Validations of the experimental results for all investigated thermophysical properties of pure *p*-xylene are reported in Ref. 36. No pure component property data of SnEHA appear to be available in the literature, so that such a comparison cannot be made here for its properties.

2.2.1 Density and Viscosity

The density ρ and viscosity η were measured using a combined instrument (SVM 3000, Anton Paar), comprising a vibrating-U-tube densimeter and a rotational viscosimeter. The combined expanded uncertainty of the density measurement was $U(\rho) = 1$ kg m⁻³ ($k = 2$). The relative combined expanded uncertainty of the viscosity measurement was $U_{\text{rel}}(\eta) = 0.02$ ($k = 2$). The manufacturer specified an uncertainty of $u(T) = 0.05$ K for the temperature (T) measurement. The proper operation of the instrument was verified by measuring certified density and viscosity standards (N.8, S6, and S200, purchased from Paragon Scientific). Before the samples were introduced to the instrument, they were degassed in an ultrasonic bath for at least ten minutes.

2.2.2 Thermal Conductivity and Isobaric Heat Capacity

The thermal conductivity λ and the thermal diffusivity a were measured using a transient hot-wire thermal conductivity meter (LAMBDA, flucon fluid control). From these experimental results, the isobaric heat capacity c_p can be calculated from Eq. (3) if the sample density ρ is known:

$$c_p = \frac{\lambda}{a \rho} \quad (3)$$

The samples were thermostatted in a double-walled vessel. The temperature in the measurement cell was measured with a Pt100 resistance thermometer calibrated against a reference thermometer certified by Physikalisch-Technische Bundesanstalt Braunschweig (PTB), which provided an uncertainty of $u(T) = 0.1$ K for the temperature measurement. The combined expanded relative uncertainty of the thermal conductivity was $U_{\text{rel}}(\lambda) = 0.04$ ($k = 2$) as reported by the manufacturer and confirmed by comparison with literature data for ethanol (see Appendix A) and *p*-xylene [36]. From error propagation, the combined expanded relative uncertainty of the isobaric heat capacity was estimated to be $U_{\text{rel}}(c_p) = 0.06$ ($k = 2$) and, again, this estimate was confirmed by comparison with literature data.

2.2.3 Self-Diffusion Coefficients

The self-diffusion coefficients were determined by ^1H NMR spectroscopy with pulsed field gradients following the procedures described in more detail by Bellaire et al. [40, 41]. The NMR spectrometer was equipped with an Ascend 400 magnet and an Avance III HD 400 console (both by Bruker) and provided a magnetic field strength of 9.4 T. The spectrometer's temperature sensor was calibrated using a Pt100 resistance thermometer calibrated against a reference thermometer certified by PTB, providing an uncertainty of $u(T) = 0.1$ K for the temperature measurement. The self-diffusion coefficients were measured by a stimulated spin-echo technique with bipolar pulsed gradients using the pulse sequence *stebpgp1s*. The self-diffusion coefficients were calculated from the Stejskal-Tanner [42] equation:

$$\ln\left(\frac{I}{I_0}\right) = -D_i \varrho^2 \delta^2 g^2 \left(\Delta - \frac{1}{3}\delta - \frac{1}{2}\zeta\right) \quad (4)$$

Here, I is the signal intensity, I_0 is the signal intensity without a gradient, D_i is the self-diffusion coefficient of component i , ϱ is the gyromagnetic ratio, δ is the duration of the application of the field gradient, g is the field gradient strength, Δ is the so-called diffusion time, and ζ is a correction constant due to the use of bipolar gradients. The value of D_i was obtained from a fit of the natural logarithm of the relative intensity $\frac{I}{I_0}$ as a function of the squared field gradient g^2 . For details see Refs. 40 and 41. The combined expanded uncertainty of the self-diffusion coefficient $U(D_i)$ from the fit to the experimental NMR data using Eq. (4) is typically about $U_{\text{rel}}(D_i) = 0.01$ ($k = 2$) but can be higher depending on composition and temperature. It is therefore stated explicitly for each individual experimental data point.

2.2.4 Vapor-Liquid Equilibria

Isobaric vapor-liquid equilibria (VLE) of binary mixtures of EHA and ethanol were measured in a recirculating still glass apparatus, which is described in more detail in Ref. 43. The apparatus is an improved version of that designed by Rafflenbeul and Hartmann [44]. Measurements were performed at 20, 40, 60, and 80 kPa and temperatures up to 400 K. It is not possible to measure VLE at temperatures above 400 K with that setup. The pressure in the measurement cell was measured with a WIKA P-30 pressure sensor with a standard uncertainty of $u(p) = 0.05$ kPa. The equilibrium temperature was measured with a Pt100 resistance thermometer that was calibrated against a PTB-certified reference thermometer. While the calibrated thermometer provides a standard uncertainty better than 0.1 K, the uncertainty of the equilibrium temperature $u(T)$ is higher due to fluctuations during the measurement and is specified here together with the experimental results.

Isobaric VLE of binary mixtures of EHA and *p*-xylene were measured with a co-current thin-film evaporator as described in Refs. 43, 45, 46. The pressure was measured using a pressure sensor of type VSR53DL by Thyracont, and the temperature was measured using a Pt100 resistance thermometer which was calibrated against a standard certified by PTB. The standard uncertainties of the temperature and pressure measurements were $u(T) = 0.1$ K and $u(p) = 0.1$ kPa, respectively.

For both binary systems, the compositions of the liquid phase and the condensed gas phase were determined from an analysis of corresponding samples by gas chromatography using an Agilent 7890A system equipped with a flame ionization detector and a Zebron Phenomenex ZB-FFAP (30 m $\times$ 0.32 mm $\times$ 0.5 μ m) column. 1,4-Dioxane was used as an internal standard. From the analysis of gravimetrically prepared samples, the standard uncertainty of the mole fraction was estimated to be $u(x) = u(y) = 0.01$ mol mol⁻¹.

2.2.5 Liquid-Liquid Equilibria

For investigating the liquid-liquid equilibria (LLE) in the system (EHA + ethanol + water), nine samples of different initial composition were prepared for each point in the temperature series. 10 g of each sample were prepared in 30 ml screw-top vials with septum. After the gravimetric preparation of the feed samples, a magnetic stirrer was added to each vial. From error propagation of the uncertainty of the weighing, the uncertainty of the mole fraction x of these samples was estimated to be $u(x) = 0.0003$ mol mol⁻¹.

The samples were kept in a temperature control cabinet (Mettler GmbH, type ICP 600), where they were stirred on a stirring plate (Variomag, Multipoint 15) at 600 rpm

for 24 h. The temperature was monitored using a Pt100 resistance thermometer in an additional vial on the stirring plate. The thermometer was calibrated against a Pt25 standard thermometer certified by PTB. The standard uncertainty of the temperature measurement was estimated to be $u(T) = 0.1$ K.

Phase separation by gravitation alone was found to be slow. Therefore, samples were transferred to 15 ml centrifuge tubes, and the phases were separated by centrifugation at 4500 rpm for 10 min using a Thermo Scientific Heraeus Multifuge X1R. The samples were held at constant temperature during centrifugation; however, the maximum possible temperature setting of the centrifuge was 313 K. Therefore, the samples from the measurement series at 323 and 333 K were put back into the tempering cabinet for one and two hours, respectively, before drawing samples from the phases.

After phase separation, samples of each phase were drawn with syringes. First, a sample was taken from the upper EHA-rich phase. When taking a sample from the lower water-rich phase, air was first drawn into the syringe and then continuously expelled while moving through the upper phase. After the sample was taken from the lower phase, liquid was continuously expelled from the syringe to prevent contamination of the sample by the upper phase. The collected samples were filled into separate screw-top vials.

The compositions of the samples from the two liquid phases were analyzed by gas chromatography using an Agilent Technologies 7890A system equipped with a thermal conductivity detector and an Agilent Technologies RTx-Wax (30 m $\times$ 0.32 mm $\times$ 1 μ m) column. 1,4-Dioxane was used as an internal standard. From analyzing gravimetrically prepared samples, the standard uncertainty of the mole fraction of all components determined by gas chromatography was estimated to be $u(x) = 0.01$ mol mol⁻¹. The detection limits of EHA, ethanol, and water were estimated to be 0.0005, 0.003, and 0.01 mol mol⁻¹, respectively.

In order to determine the stirring time needed for achieving reproducible LLE results, preliminary investigations of the LLE in the binary system (EHA + water) were conducted at 298 K. No differences beyond measurement uncertainty of the phase compositions were observed between samples analyzed after stirring times of 24 hours and one, two, three, and four weeks. Hence, a stirring time of 24 hours was chosen for all experimental results reported in Chapter 7.

Furthermore, in a brief preliminary study, the esterification reaction between EHA and ethanol was investigated. In the absence of a catalyzing acid, only minute amounts of the ester were detected by NMR spectroscopy even after several months (see Appendix D). Therefore, the esterification reaction was found to be negligible and not further considered in this work.

3 Modeling of Thermophysical Properties

3.1 Density, Thermal Conductivity, Heat Capacity, Viscosity, and Self-Diffusion Coefficients

The results for the density, the thermal conductivity, and the isobaric heat capacity were correlated using Redlich-Kister-type polynomials [47], as used successfully in Refs. 36–39 and the literature [48–50]. The approach is illustrated using the exemplary mixture property z , which is a function of the pure component properties z_i^{pure} , the mole fractions of the components x_i ($i = 1, 2$), and an excess term z^{E} here:

$$z = x_1 z_1^{\text{pure}} + x_2 z_2^{\text{pure}} + z^{\text{E}} \quad (5)$$

A polynomial with the adjustable parameters $a_{i,z}$, $b_{i,z}$, and $c_{i,z}$ was used to describe the temperature dependence of the pure component properties z_i^{pure} , where $[z]$ is the unit of z :

$$z_i^{\text{pure}}/[z] = a_{i,z} + b_{i,z} T/\text{K} + c_{i,z} (T/\text{K})^2 \quad (6)$$

The excess contribution was modeled as follows, using the adjustable parameters E_z , F_z , and G_z :

$$z^{\text{E}}/[z] = (E_z + F_z T/\text{K} + G_z x_1 x_2) x_1 x_2 \quad (7)$$

Instead of modeling the results for the density ρ directly, a correlation for the molar volume v is presented, where

$$v = \frac{\bar{M}}{\rho}. \quad (8)$$

Therein, $\bar{M}$ is the average molar mass:

$$\bar{M} = x_1 M_1 + x_2 M_2. \quad (9)$$

M_1 and M_2 are the molar masses of the components.

For modeling the viscosity in mixtures of EHA and ethanol, the same approach as for the density, thermal conductivity, and isobaric heat capacity was chosen and a Redlich-Kister-type polynomial was used (see Eq. (5)). For modeling the viscosity in mixtures of EHA or SnEHA (x_1) and *p*-xylene (x_2), the Jouyban-Acree correlation [51] was used to correlate the mixture viscosity, as in Keller et al. [36, 39]:

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

In all cases, the temperature dependence of the pure component viscosities η_i^{pure} was described by an exponential function with the adjustable parameters $a_{i,\eta}$, $b_{i,\eta}$, and $c_{i,\eta}$.

$$\eta_i^{\text{pure}} / \text{mPa s} = a_{i,\eta} \exp \left(\frac{b_{i,\eta}}{T/\text{K}} \right) + c_{i,\eta} \quad (11)$$

The self-diffusion coefficients in mixtures of EHA and ethanol or *p*-xylene were modeled using an empirical polynomial equation (Eq. (12)) based on the approach of Keller et al. [36]. However, for describing these experimental data, a cubic term with respect to the mole fraction was found to give better results than the quadratic term used in Ref. 36. Furthermore, a better description of the data is obtained if the mole fraction of ethanol or *p*-xylene (x_2) is used instead of the mole fraction of the diffusing component x_i :

$$D_i / (10^{-9} \text{ m}^2 \text{ s}^{-1}) = a_{i,D_i} + b_{i,D_i} T/\text{K} + (c_{i,D_i} + d_{i,D_i} T/\text{K}) x_2 + (e_{i,D_i} + f_{i,D_i} T/\text{K}) x_2^3. \quad (12)$$

Therein, $a_{i,D_i} - f_{i,D_i}$ are adjustable parameters.

By contrast, for modeling the self-diffusion coefficients in mixtures of SnEHA and *p*-xylene, the following different approach was found to better represent the data:

$$D_i / (10^{-9} \text{ m}^2 \text{ s}^{-1}) = \left(a_{i,D_i} \exp \left(-b_{i,D_i} \frac{T_{\text{ref}}}{T} \right) \right)^{x_i} \left(c_{i,D_i} \exp \left(-d_{i,D_i} \frac{T_{\text{ref}}}{T} \right) \right)^{1-x_i} (e_{i,D_i})^{(1-x_i)x_i} \quad (13)$$

Therein, the adjustable parameters a_{i,D_i} and b_{i,D_i} describe the temperature-dependent self-diffusion coefficient of the pure component i (D_i^{pure}). The adjustable parameters c_{i,D_i} and d_{i,D_i} describe the temperature-dependent self-diffusion coefficient of component i at infinite dilution in component j ($D_{i,j}^\infty$). e_{i,D_i} is an additional adjustable parameter. $T_{\text{ref}} = 298.15 \text{ K}$ is a reference temperature introduced to reduce the magnitude of the obtained fit parameters b_{i,D_i} and d_{i,D_i} .

The adjustable parameters of all empirical correlations mentioned above were regressed using the python functions `numpy.polyfit` and `scipy.optimize.curve_fit`.

The objective function (OF) for the optimization was the squared sum of deviations between the experimental (exp) and the correlation (calc) results:

$$\text{OF}_z = \sum_{l=1}^{N_{\text{exp}}} (z_l^{\text{exp}} - z_l^{\text{calc}})^2 \quad (14)$$

Therein, N_{exp} is the number of experimental data points measured for property z .

3.2 Mutual Diffusion Coefficients

The correlations for the self-diffusion coefficients (see Eqs. (12) and (13)) were used for the extrapolation to infinite dilution. At infinite dilution, the self-diffusion coefficients become equal to the Maxwell-Stefan diffusion coefficients $D_{i,j}^{\infty}$ and $D_{j,i}^{\infty}$ in binary mixtures of components i and j . The Vignes correlation [52] was then used for calculating the Maxwell-Stefan diffusion coefficient D over the entire composition range:

$$D = (D_{i,j}^{\infty})^{x_j} (D_{j,i}^{\infty})^{x_i} \quad (15)$$

The Fickian diffusion coefficient D was then calculated using the Maxwell-Stefan diffusion coefficient and the thermodynamic factor Γ :

$$D = D\Gamma, \quad (16)$$

where Γ is

$$\Gamma = 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_i} \quad (17)$$

in a binary system. The activity coefficients γ_i and their derivatives were modeled as described in Section 3.4.

3.3 Lewis Number

The Lewis number Le (cf. Eq. (1)) was calculated from the thermal diffusivity a and the binary Fickian diffusion coefficient D . The thermal diffusivity a (cf. Eq. (2)) was calculated using the correlations for the thermal conductivity, the molar volume, and the isobaric heat capacity (see Section 3.1). The Fickian diffusion coefficient was calculated as described in Section 3.2.

3.4 Phase Equilibria

The VLE were modeled based on the extended Raoult's law assuming the gas phase to be ideal and neglecting the pressure dependence of the chemical potential in the liquid phase:

$$p_i^s x_i \gamma_i = p y_i \quad (18)$$

Therein, p_i^s is the vapor pressure of the pure component i , x_i is the liquid phase mole fraction of component i , γ_i is the activity coefficient of component i normalized according to Raoult, p is the pressure, and y_i is the gas phase mole fraction of component i . The pure component vapor pressures p_i^s were calculated from the following Antoine-type equation with the empirical parameters A_i , B_i , and C_i , which were obtained from fits to literature data:

$$\ln(p_i^s / \text{kPa}) = A_i + \frac{B_i}{T/\text{K} + C_i} \quad (19)$$

For modeling the LLE in mixtures of EHA, ethanol, and water, the isoactivity criterion was used:

$$x'_i \gamma'_i = x''_i \gamma''_i. \quad (20)$$

Herein, x'_i and x''_i are the mole fractions of component i in the EHA-rich phase (') and in the water-rich phase ("), and γ'_i and γ''_i are the corresponding activity coefficients normalized according to Raoult.

For both the VLE and LLE studied in this work, the activity coefficients γ_i were modeled using the non-random two-liquid (NRTL) model [53, 54]:

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_l^N G_{li} x_l} + \sum_j^N \frac{x_j G_{ij}}{\sum_l^N G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_l^N x_l \tau_{lj} G_{lj}}{\sum_l^N G_{lj} x_l} \right), \quad (21)$$

with

$$G_{ij} = \exp(-\alpha \tau_{ij}). \quad (22)$$

N is the number of components. For the binary case, Eq. (21) reduces to:

$$\ln \gamma_i = x_j^2 \left[\tau_{ji} \left(\frac{G_{ji}}{x_i + x_j G_{ji}} \right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij})^2} \right]. \quad (23)$$

The adjustable parameters of the NRTL model are the non-randomness parameter α and the binary interaction parameters τ_{ij} . The parameter α was set to 0.3 following the recommendations in the original publication of the model [53].

While for modeling VLE, the binary interaction parameters τ_{ij} were considered to be temperature-independent, for modeling LLE, the NRTL parameters τ_{ij} were modeled

as a function of temperature

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T/\text{K}}, \quad (24)$$

with the adjustable parameters a_{ij} and b_{ij} .

For adjusting the binary interaction parameters τ_{ij} of the NRTL model to the VLE data, the objective function was the sum of the squared deviations between measured (exp) and calculated (calc) pressures p_j .

$$\text{OF}_{\text{VLE}} = \sum_{l=1}^{N_{\text{exp}}} (p_j^{\text{exp}} - p_j^{\text{calc}})^2 \quad (25)$$

Therein, N_{exp} is the number of experimental VLE data points. The results for the composition of the gas phase were not used as it contains predominantly the low-boiling component in the pressure range where experiments were possible. The python solver `scipy.optimize.curve_fit` was used to fit the adjustable parameters.

The objective function for correlating the LLE data, in both the binary and ternary cases, was the squared deviation between the experimental data (exp) and the calculated model results (calc):

$$\text{OF} = \sum_l^{N_{\text{exp}}} \sum_i^N (x'_{i,l,\text{exp}} - x'_{i,l,\text{calc}})^2 + (x''_{i,l,\text{exp}} - x''_{i,l,\text{calc}})^2, \quad (26)$$

where N_{exp} is the number of experimental LLE data points.

To ensure that the solutions of the parameter fits yield stable LLE compositions, i.e., that the results are consistent with a minimum of the Gibbs energy of mixing, an additional constraint was applied in the optimization. Each tie line has to satisfy the positive tangent plane distance criterion [55, 56]: the Gibbs energy of mixing along the tie line has to be smaller than that on the Gibbs energy surface above it. The method was implemented as described in Ref. 55.

For the numerical evaluation of the LLE, the mole fractions of each component in the two phases in thermodynamic equilibrium were calculated using the Rachford-Rice algorithm [57–59].

All calculations were implemented in python, employing the functions `minimize`, `root`, and `curve_fit` from the `scipy.optimize` package for the optimization procedures.

4 Thermophysical Properties of Mixtures of (EHA + Ethanol)

4.1 State of the Art

Mixtures of EHA and ethanol are common solvents in precursor solutions for the spray flame synthesis of nanoparticles, especially in combination with metal nitrates as low-cost metal-containing precursors. [10, 26, 60–64] Property data are widely available for pure ethanol. For pure EHA, only some measurements of the vapor pressure [65–73], enthalpy of vaporization [71, 74, 75], and density at atmospheric pressure [74] as well as along the saturation line [71] have been reported. The viscosity was measured at 298.15, 313.15 and 373.15 K [76]. Furthermore, data on critical properties [71, 77, 78] as well as on the enthalpy of formation [74] and two-phase heat capacities [71] of EHA are available. No data are available in the literature for mixtures of EHA and ethanol; hence, they were measured in the present work.

4.2 Density

The experimental results for the density of mixtures of EHA and ethanol are shown in Table 2 and are depicted in Figure 1 together with the model results. Pure EHA has a higher density than pure ethanol and thus, the mixture density decreases with increasing ethanol mole fraction x_{EtOH} . As expected, the density decreases with increasing temperature. The molar volume decreases almost linearly with increasing ethanol mole fraction and the molar excess volume is small compared to the overall molar volume. Thus, binary mixtures of ethanol and EHA behave approximately ideally with respect to the molar volume.

Table 2: Density ρ , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties are $U(\rho) = 1 \text{ kg m}^{-3}$ ($k = 2$), $U(x_{\text{EtOH}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), $u(p) = 3 \text{ kPa}$, and $u(T) = 0.05 \text{ K}$.

T / K	$\rho / \text{kg m}^{-3}$				
	$x_{\text{EtOH}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1
293.15	906.4	895.0	878.5	849.2	789.4
303.15	898.2	886.8	870.1	840.9	780.9
313.15	890.0	878.5	861.9	832.5	772.1
323.15	882.0	870.3	853.5	823.9	763.2
333.15	873.8	862.0	844.8	815.1	753.8

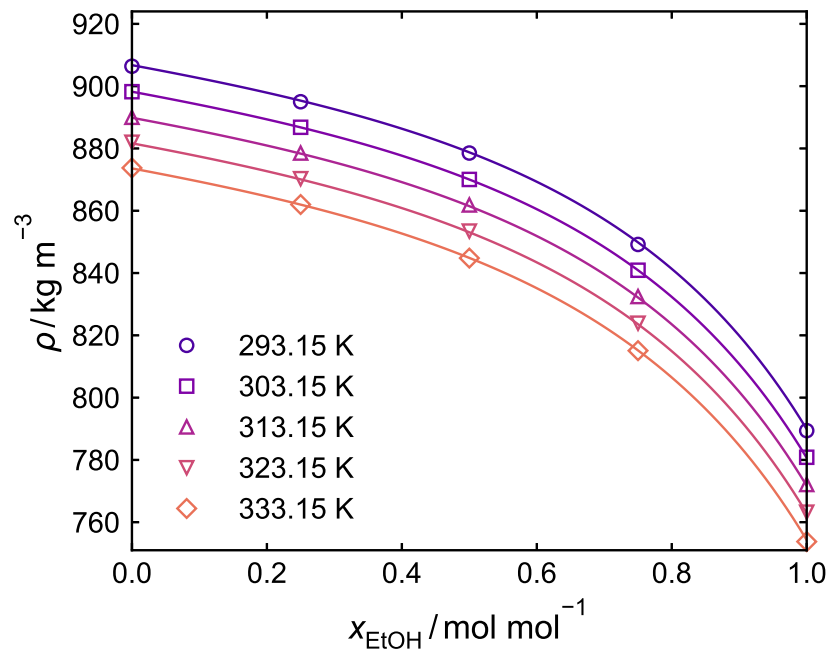


Figure 1: Density ρ of mixtures of EHA and ethanol at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations, cf. Eqs.(6) – (8), and (7), with parameters listed in Tables 9 and 10.

4.3 Viscosity

Table 3 contains the experimental results for the mixture viscosities at different temperatures. Figure 2 depicts the measured and modeled viscosities as a function of the mixture composition at different temperatures. As expected, the viscosity decreases with increasing temperature. Pure EHA has a significantly higher viscosity than pure ethanol. Consequently, the viscosity of the mixtures of EHA and ethanol decreases with increasing ethanol content. The roughly linear relationship between viscosities at different compositions is rather unusual. The systems studied by Keller et al. [36, 37, 38, 39] show a strong non-ideality of the mixture viscosity and a more complex model was necessary to describe the data.

Table 3: Viscosity η , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties are given in the table for $U(\eta)$ and $U(x_{\text{EtOH}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.05$ K.

T / K	$\eta / \text{mPa s} \ (U(\eta) / \text{mPa s})$				
	$x_{\text{EtOH}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1
293.15	7.529 (0.146)	5.978 (0.050)	4.430 (0.039)	2.646 (0.025)	1.198 (0.010)
303.15	5.354 (0.046)	4.328 (0.037)	3.292 (0.028)	2.080 (0.020)	0.991 (0.009)
313.15	3.961 (0.034)	3.257 (0.028)	2.531 (0.021)	1.661 (0.014)	0.825 (0.013)
323.15	3.042 (0.026)	2.531 (0.021)	1.996 (0.017)	1.349 (0.011)	0.671 (0.025)
333.15	2.413 (0.021)	2.022 (0.017)	1.611 (0.015)	1.096 (0.027)	0.570 (0.042)

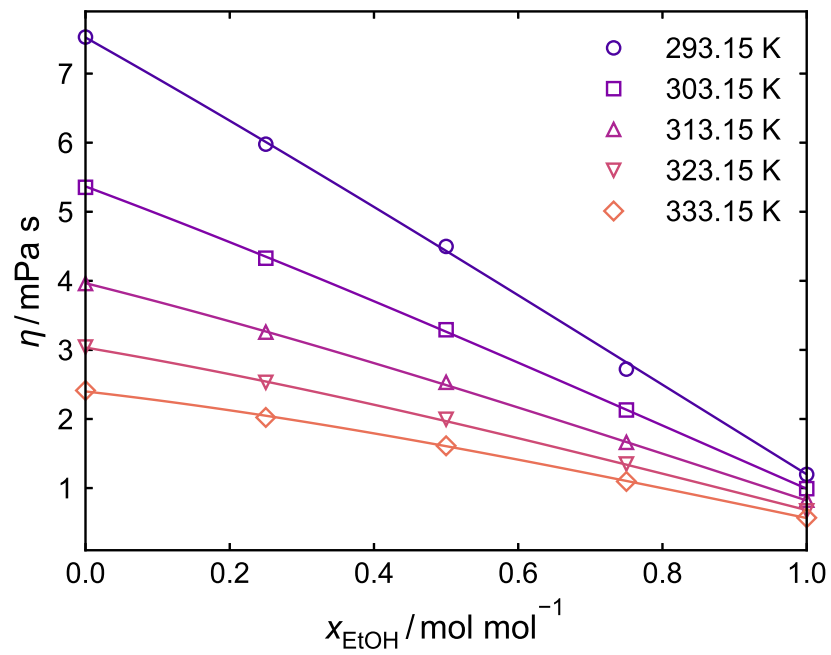


Figure 2: Viscosity η of mixtures of EHA and ethanol at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations, cf. Eqs. (5), (7), and (11), with parameters listed in Tables 9 and 10.

4.4 Thermal Conductivity

The results of the thermal conductivity measurements are given in Table 4 and are depicted in Figure 3 together with the model results. The thermal conductivities of both pure components and of all mixtures decrease with increasing temperature. Pure EHA has a lower thermal conductivity than pure ethanol. Thus, the mixture thermal conductivity increases with increasing ethanol mole fraction. A similar behavior is found, for example, for mixtures of ethanol with ethyl acetate [79] and with cyclohexane [80].

Table 4: Thermal conductivity λ , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the thermal conductivity is $U_{\text{rel}}(\lambda) = 0.04$ ($k = 2$) and the other combined expanded uncertainties are $U(x_{\text{EtOH}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$\lambda / \text{W m}^{-1} \text{K}^{-1}$				
	$x_{\text{EtOH}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1
293.15	0.139	0.143	0.149	0.157	0.171
303.15	0.138	0.141	0.147	0.155	0.169
313.15	0.136	0.141	0.146	0.154	0.167
323.15	0.135	0.139	0.144	0.152	0.164
333.15	0.133	0.136	0.142	0.150	0.162

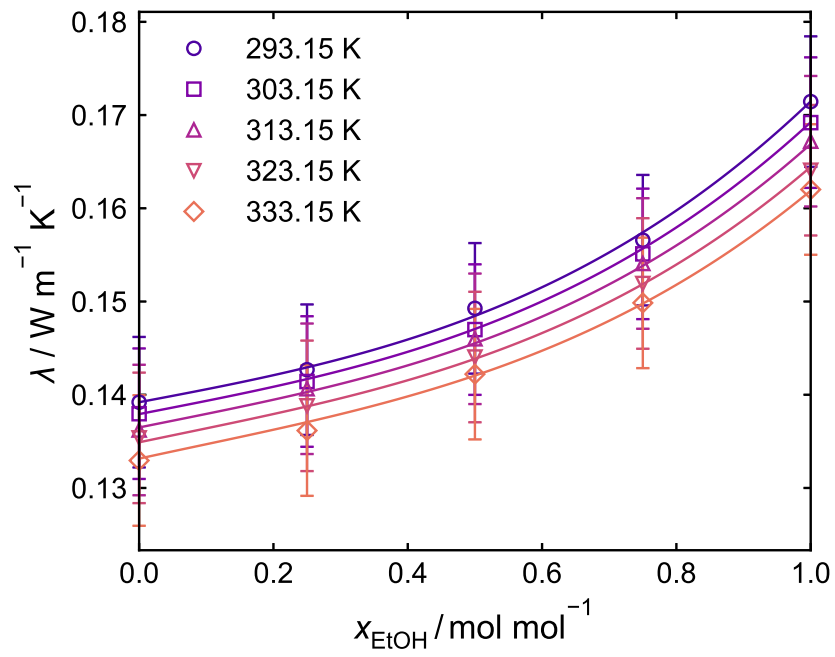


Figure 3: Thermal conductivity λ of mixtures of EHA and ethanol at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations, cf. Eqs. (5), (6), and (7), with parameters listed in Tables 9 and 10.

4.5 Isobaric Heat Capacity

The results of the isobaric heat capacity measurements are given in Table 5 and are depicted in Figure 4 together with the model results. Pure EHA has a significantly higher isobaric heat capacity than pure ethanol. The isobaric heat capacity of mixtures of EHA and ethanol decreases almost linearly with the ethanol content and increases with increasing temperature. Hence, as for many mixtures investigated by Keller et al. [36, 37, 38, 39], the excess heat capacity is small.

Table 5: Isobaric heat capacity c_p , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the isobaric heat capacity is $U_{\text{rel}}(c_p) = 0.06$ ($k = 2$) and the other combined expanded uncertainties are $U(x_{\text{EtOH}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$c_p / \text{J mol}^{-1} \text{K}^{-1}$				
	$x_{\text{EtOH}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1
293.15	256	220	185	148	112
303.15	261	224	187	150	114
313.15	265	229	191	154	116
323.15	271	233	194	156	117
333.15	274	235	198	159	120

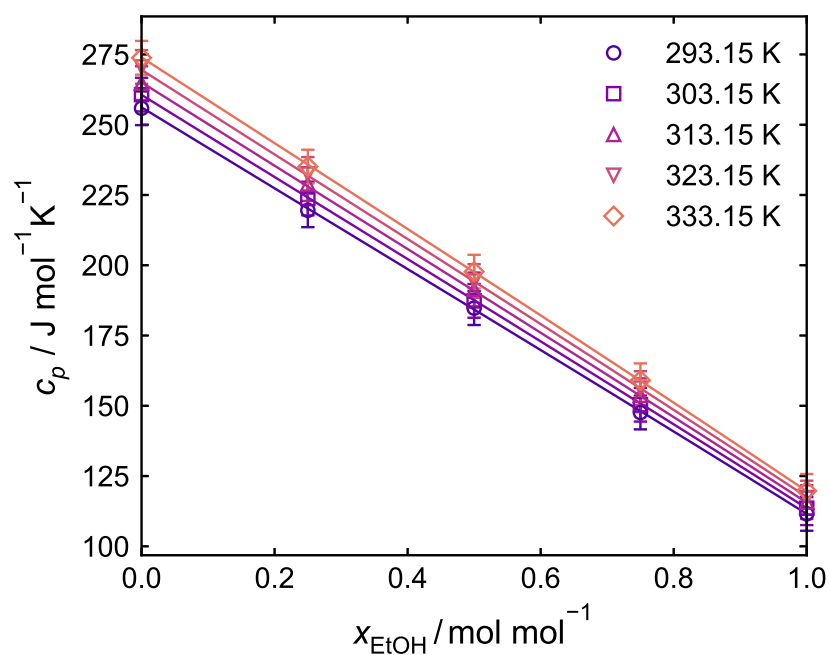


Figure 4: Isobaric heat capacity c_p of mixtures of EHA and ethanol at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations, cf. Eqs. (5), (6), and (7), with parameters listed in Tables 9 and 10.

4.6 Self-Diffusion Coefficients

The results for the self-diffusion coefficients of pure EHA and pure ethanol as well as of EHA and ethanol in mixtures of EHA and ethanol are given in Tables 6 and 7, respectively. The experimental results together with those of the empirical correlation are depicted in Figure 5. As expected, since EHA is a larger molecule and has a higher viscosity than ethanol, its self-diffusion coefficient is generally lower than that of ethanol. Consequently, the self-diffusion coefficients of EHA and ethanol increase with increasing temperature and increasing ethanol content in the mixture. The strongly nonlinear behavior with respect to the composition is in agreement with experimental and simulation results for other binary systems [40, 81].

Table 6: Self-diffusion coefficient D_{EHA} , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{EHA}})$ ($k = 2$) are given in the table and $U(x_{\text{EtOH}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

		$D_{\text{EHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1} \ (U(D_{\text{EHA}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1})$			
		$x_{\text{EtOH}} / \text{mol mol}^{-1}$			
T / K	0	0.258	0.503	0.75	0.98
298.15	0.126 (0.001)	0.164 (0.001)	0.219 (0.002)	0.337 (0.002)	0.598 (0.022)
313.15	0.213 (0.001)	0.267 (0.002)	0.338 (0.007)	0.490 (0.016)	0.877 (0.006)
333.15	0.375 (0.001)	0.443 (0.018)	0.550 (0.034)	0.753 (0.092)	1.323 (0.007)

Table 7: Self-diffusion coefficient D_{EtOH} , liquid mole fraction x_{EtOH} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{EtOH}})$ ($k = 2$) are given in the table and $U(x_{\text{EtOH}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

		$D_{\text{EtOH}} / 10^{-9} \text{ m}^2 \text{ s}^{-1} \ (U(D_{\text{EtOH}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1})$			
		$x_{\text{EtOH}} / \text{mol mol}^{-1}$			
T / K	0.02	0.258	0.503	0.75	1
298.15	0.240 (0.001)	0.276 (0.001)	0.366 (0.001)	0.567 (0.001)	1.071 (0.001)
313.15	0.376 (0.045)	0.463 (0.003)	0.577 (0.009)	0.844 (0.016)	1.494 (0.002)
333.15	0.716 (0.023)	0.789 (0.023)	0.987 (0.043)	1.331 (0.096)	2.251 (0.006)

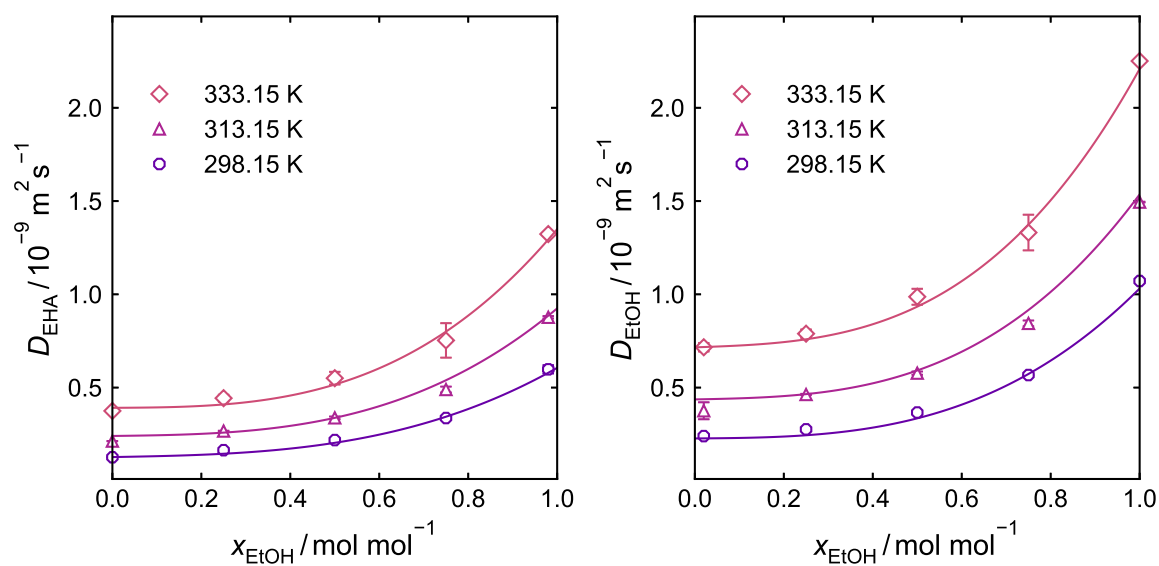


Figure 5: Self-diffusion coefficients of EHA (left) and ethanol (right) in mixtures of EHA and ethanol at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations, cf. Eq. (12), with parameters listed in Table 11.

4.7 Vapor-Liquid Equilibrium

The results of the VLE measurements are given in Table 8. Figure 6 depicts the experimental as well as the model results for the VLE of mixtures of ethanol and EHA at 20, 40, 60, and 80 kPa. Due to the temperature limitation of 400 K of the experimental setup, it was not possible to obtain VLE data over the entire liquid phase composition range for $p > 40$ kPa. The system (EHA + ethanol) shows a zeotropic behavior with ethanol as the low-boiling and EHA as the high-boiling component. Due to the large difference in pure component boiling temperatures at all pressures, ethanol is the main component in the vapor phase over a wide concentration range. Thus, during the evaporation of an (EHA + ethanol) droplet in a hot atmosphere, as found in processes such as spray flame synthesis, ethanol will evaporate from the droplet surface preferentially. Significant amounts of EHA will only be found in the gas phase around an evaporating droplet once the ethanol mole fraction x_{EtOH} at the droplet surface is less than approximately 0.25 mol mol⁻¹, where the mixture boiling temperature increases steeply with decreasing ethanol content. Consequently, further evaporation of ethanol leads to a strong increase of the droplet temperature. If the liquid phase mass transfer is slow compared to the heat transfer, superheating in some parts of the droplet could occur and cause droplet micro-explosions.

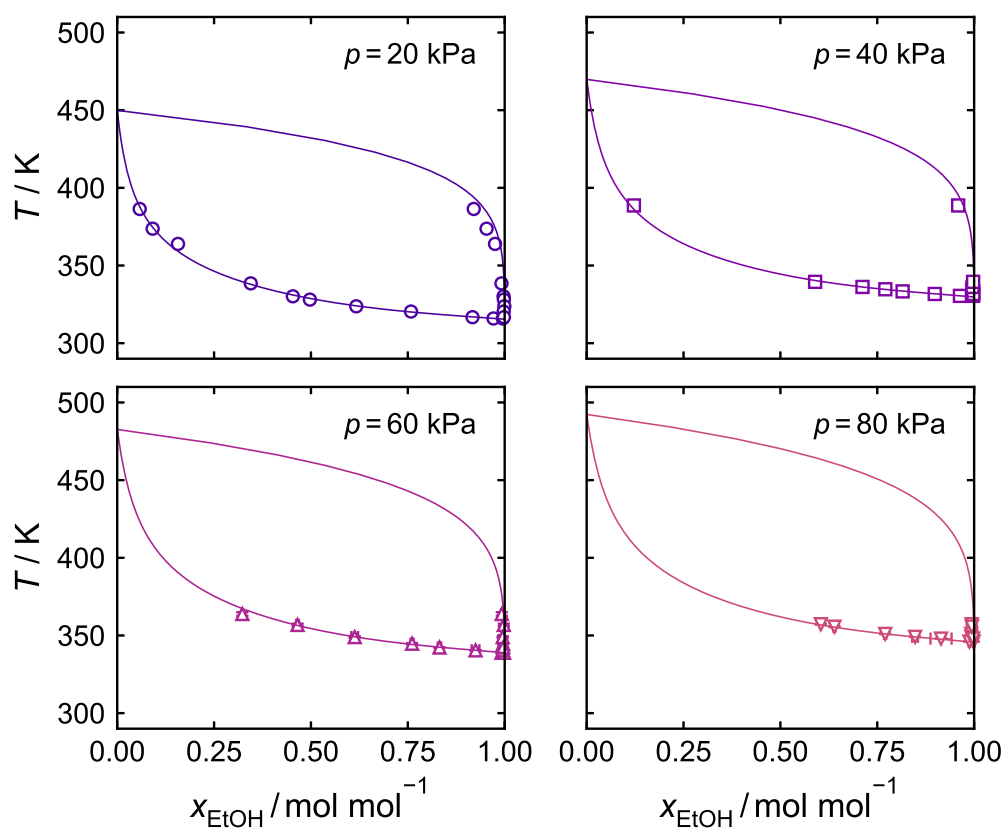


Figure 6: VLE of mixtures of EHA and ethanol. Symbols are experimental results. Error bars indicate the experimental standard uncertainty. Lines show modeling results using the extended Raoult's law with activity coefficients from NRTL, cf. Eqs. (18), (19) and (23) and parameters from Tables 12 and 13.

Table 8: Results of the isobaric VLE measurements: pressure p , temperature T , liquid phase mole fraction x_{EtOH} , and vapor phase mole fraction y_{EtOH} . The standard uncertainties are $u(p) = 0.05$ kPa, $u(T) = 1$ K, and $u(x_{\text{EtOH}}) = u(y_{\text{EtOH}}) = 0.01$ mol mol⁻¹.

p / kPa	T / K	x_{EtOH} / mol mol ⁻¹	y_{EtOH} / mol mol ⁻¹
20	315.9	0.971	0.995
	316.7	0.917	0.998
	320.4	0.758	0.997
	323.7	0.617	0.999
	328.0	0.497	0.998
	330.2	0.453	0.997
	338.5	0.345	0.992
	363.9	0.157	0.975
	373.7	0.091	0.953
	386.4	0.058	0.920
40	330.5	0.963	0.997
	331.7	0.898	0.998
	333.3	0.815	0.998
	334.7	0.771	0.995
	336.2	0.712	0.996
	339.5	0.590	0.997
	388.7	0.122	0.959
60	338.9	0.992	0.998
	340.4	0.925	0.995
	342.3	0.832	0.996
	344.7	0.761	0.996
	349.0	0.613	0.995
	356.8	0.465	0.998
	363.8	0.323	0.993
80	346.1	0.988	0.999
	348.0	0.915	0.997
	349.1	0.848	0.993
	351.0	0.770	0.992
	355.7	0.639	0.994
	357.2	0.604	0.994

4.8 Lewis Number

Figure 7 shows the Lewis number of mixtures of EHA and ethanol as a function of composition at different temperatures. The Lewis number decreases with increasing temperature. The largest values are obtained for high concentrations of EHA. A local minimum is found at around $x_{\text{EtOH}} = 0.8 \text{ mol mol}^{-1}$. To the right of the minimum, the Lewis number increases but slightly. Overall, the Lewis number is very high, indicating that the heat transport is much faster than the diffusive mass transport in mixtures of EHA and ethanol.

Due to the relatively slow mass transport and the wide-boiling VLE, EHA will tend to accumulate at the droplet surface during droplet evaporation. If the temperature continues to rise inside of the droplet, as promoted by the comparatively fast heat transfer, superheating can occur in the droplet interior, as will be shown for mixtures of TTIP and *p*-xylene in Chapter 8. Eventually, this superheating can lead to droplet micro-explosions.

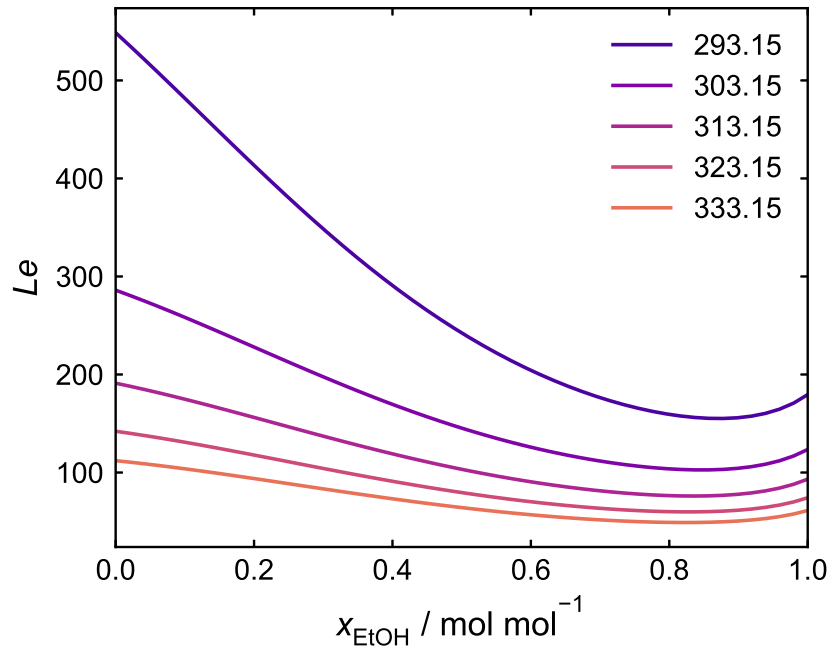


Figure 7: Lewis number Le of mixtures of EHA and ethanol at 101.3 kPa and different temperatures.

4.9 Parameters

The parameters $a_{i,z}$, $b_{i,z}$, and $c_{i,z}$ for the correlations for the pure component properties (Eqs. (6) and (11)) are given in Table 9. Table 10 lists the values of the parameters E_z , F_z , and G_z of the excess property correlations (Eq. (7)). Table 11 lists the parameters for the empirical correlation (Eq. (12)) for the self-diffusion coefficients. The parameters of the Antoine equation (19) for the pure component vapor pressures as obtained from a fit to literature data are given in Table 12. The NRTL parameters, which were determined from a fit of the present experimental data to the VLE model (Eqs. (18), (23), and (22)), are given in Table 13.

Table 9: Parameters of the correlations for the pure-component properties of EHA and ethanol.

property z	Eq.	$a_{i,z}$	$b_{i,z}$	$c_{i,z}$
$v_{\text{EHA}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	1.1481×10^{-4}	1.5090×10^{-7}	0 ^a
$\eta_{\text{EHA}}^{\text{pure}} / \text{mPa s}$	(11)	7.4089×10^{-5}	3.3525×10^3	6.6045×10^{-1}
$\lambda_{\text{EHA}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	1.0638×10^{-1}	3.4356×10^{-4}	-7.9010×10^{-7}
$c_{p,\text{EHA}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	1.2608×10^2	4.4382×10^{-1}	0 ^a
$v_{\text{EtOH}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	3.8157×10^{-5}	6.8803×10^{-8}	0 ^a
$\eta_{\text{EtOH}}^{\text{pure}} / \text{mPa s}$	(11)	1.7032×10^{-2}	1.3167×10^3	-3.2105×10^{-1}
$\lambda_{\text{EtOH}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	1.8982×10^{-1}	9.3203×10^{-5}	-5.3142×10^{-7}
$c_{p,\text{EtOH}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	5.2409×10^1	2.0175×10^{-1}	0 ^a

^aNot needed and set to zero.

Table 10: Parameters of the correlations for the excess properties of mixtures of EHA and ethanol (see Eq. (7)).

property z	E_z	F_z	G_z
$v / \text{m}^3 \text{ mol}^{-1}$	-1.7280×10^{-7}	-5.0957×10^{-9}	-1.2009×10^{-6}
$\eta / \text{mPa s}$	-1.2335	5.1935×10^{-3}	-1.4577×10^{-1}
$\lambda / \text{W m}^{-1} \text{ K}^{-1}$	-6.9158×10^{-2}	1.4201×10^{-4}	-8.8192×10^{-3}
$c_p / \text{J mol}^{-1} \text{ K}^{-1}$	-1.0183×10^1	3.9976×10^{-2}	1.3266

Table 11: Parameters of the correlations for the self-diffusion coefficients (see Eq. (12)).

component	a_{i,D_i}	b_{i,D_i}	c_{i,D_i}	d_{i,D_i}	e_{i,D_i}	f_{i,D_i}
EHA	-2.1219	7.54435×10^{-3}	3.0734×10^{-1}	-8.8196×10^{-4}	-3.9162	1.4590×10^{-2}
ethanol	-3.9337	1.3956×10^{-2}	-5.3178×10^{-1}	1.8497×10^{-3}	-4.5322	1.7832×10^{-2}

Table 12: Antoine parameters for EHA and ethanol obtained from fits of Eq. (19) to the indicated literature data.

component	A_i	B_i	C_i	Ref.
EHA	1.5235×10^1	-4.0666×10^3	-1.1761×10^2	71
ethanol	1.6497×10^1	-3.5719×10^3	-5.0735×10^1	82

Table 13: NRTL parameters obtained from a fit to the present experimental data.

α	$\tau_{\text{EtOH,EHA}}$	$\tau_{\text{EHA,EtOH}}$
0.3	2.4197	-1.3430

5 Thermophysical Properties of Mixtures of (EHA + *p*-Xylene)

5.1 State of the Art

EHA and xylene are commonly used solvents in spray flame synthesis of nanoparticles. Mixtures of these components are suitable solvents for various precursors. [7, 8, 18, 25, 83–85] Moreover, when studying spray flame processes with numerical techniques, mixtures of EHA and xylene can be used as a simpler, surrogate model system for the frequently used precursor solutions containing metal 2-ethylhexanoates and xylene. [19, 27, 86, 87] In the mentioned applications, all three isomers of xylene, i.e., *o*-xylene, *m*-xylene, and *p*-xylene, occur. However, the influence of the choice of isomer on the overall spray flame process is expected to be marginal. The *p*-xylene isomer is studied in this work to maintain consistence with previous studies [36].

Despite their relevance especially in the field of spray flame synthesis, no data on the properties of mixtures of EHA and *p*-xylene appear to be available in the literature. Due to its use as an industrial solvent and intermediate [88], data on the properties of pure *p*-xylene are sufficiently available. The properties of pure EHA were extensively studied in Chapter 4.

5.2 Density

Table 14 lists the experimental results for the density. They are shown in Figure 8 together with the correlation results. As expected, the density decreases with increasing temperature and increasing *p*-xylene mole fraction. While the density has a more complex dependence on the composition, the molar volume (see Appendix B) exhibits an almost perfectly linear dependence on the *p*-xylene mole fraction, indicating an almost ideal mixing behavior.

Table 14: Density ρ , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainty of the density is $U(\rho) = 1 \text{ kg m}^{-3}$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), $u(p) = 3 \text{ kPa}$, and $u(T) = 0.05 \text{ K}$.

T / K	$\rho / \text{kg m}^{-3}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0 ^a	0.25	0.5	0.75	1
293.15	906.4	897.4	887.4	875.2	861.1
303.15	898.2	889.1	879.0	866.6	852.4
313.15	890.0	880.9	870.5	858.0	843.5
323.15	882.0	872.6	862.0	849.4	834.9
333.15	873.8	864.3	853.5	840.7	826.0
343.15	865.7	856.0	844.9	831.9	817.1
353.15	857.6	847.6	836.3	823.2	808.1

^aRepeated from Chapter 4 for the reader's convenience.

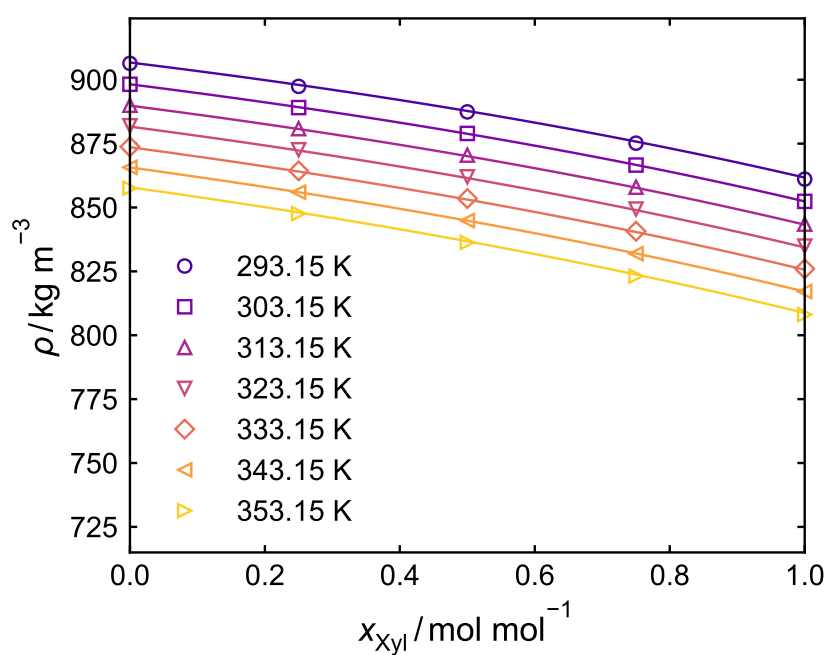


Figure 8: Density ρ of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations (cf. Eqs. (5) – (9)) with parameters listed in Tables 21 and 22.

5.3 Viscosity

Table 15 lists the experimental results for the viscosity. They are shown in Figure 9 together with the correlation results. Expectedly, the viscosity decreases strongly with increasing temperature and with increasing *p*-xylene mole fraction. In contrast to mixtures of EHA with ethanol, for which the viscosity surprisingly shows an almost linear dependence on the mole fraction (see Chapter 4), the corresponding relation is strongly nonlinear for mixtures of EHA and *p*-xylene. This is in line with previous findings for mixtures of TTIP and *p*-xylene. [36]

Table 15: Viscosity η , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the viscosity $U(\eta)$ ($k = 2$) are given in the table, and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.05$ K.

η / mPa s ($U(\eta)$ / mPa s)					
x_{Xyl} / mol mol ⁻¹					
T / K	0 ^a	0.25	0.5	0.75	1
293.15	7.529 (0.146)	3.363 (0.031)	1.754 (0.015)	1.025 (0.010)	0.664 (0.006)
303.15	5.354 (0.046)	2.606 (0.024)	1.441 (0.021)	0.881 (0.008)	0.587 (0.005)
313.15	3.961 (0.034)	2.080 (0.018)	1.218 (0.011)	0.768 (0.008)	0.515 (0.009)
323.15	3.042 (0.026)	1.702 (0.015)	1.041 (0.009)	0.678 (0.006)	0.471 (0.005)
333.15	2.413 (0.021)	1.423 (0.013)	0.904 (0.008)	0.604 (0.006)	0.427 (0.004)
343.15	1.961 (0.017)	1.210 (0.011)	0.794 (0.007)	0.546 (0.008)	0.391 (0.004)
353.15	1.629 (0.014)	1.045 (0.009)	0.705 (0.006)	0.494 (0.005)	0.360 (0.004)

^aRepeated from Chapter 4 for the reader's convenience.

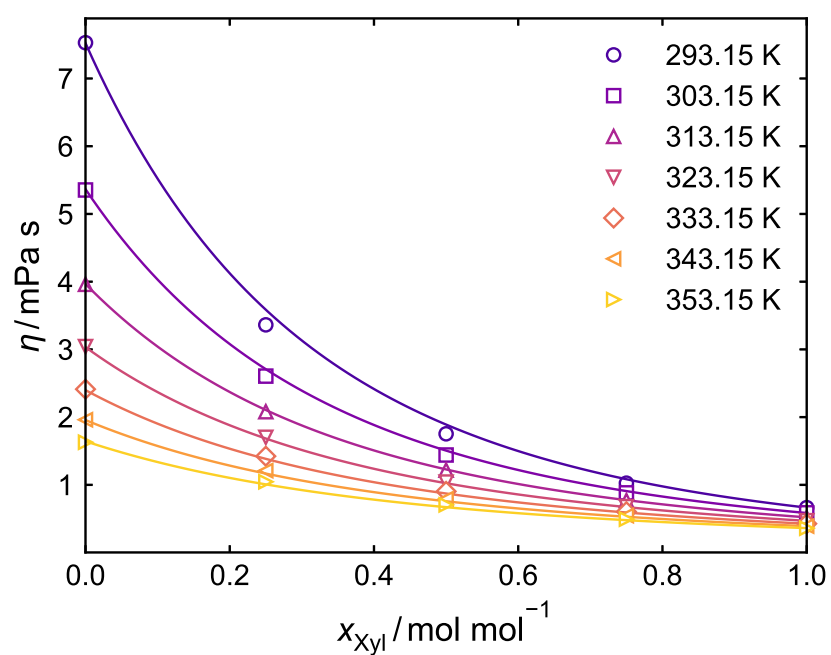


Figure 9: Viscosity η of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations (cf. Eqs. (10) and (11)) with parameters listed in Tables 21 and 22.

5.4 Thermal Conductivity

Table 16 lists the experimental results for the thermal conductivity. They are shown in Figure 10 together with the correlation results. The thermal conductivity decreases with increasing temperature and decreasing *p*-xylene mole fraction. The difference between the thermal conductivities of pure EHA and pure *p*-xylene is rather small; however, a clear deviation from linearity with respect to the composition and, thus, from ideal behavior is observed.

Table 16: Thermal conductivity λ , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the thermal conductivity is $U_{\text{rel}}(\lambda) = 0.04$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$\lambda / \text{W m}^{-1} \text{K}^{-1}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0 ^a	0.25	0.5	0.75	1
293.15	0.139	0.137	0.135	0.132	0.129
303.15	0.138	0.135	0.133	0.130	0.127
313.15	0.136	0.134	0.131	0.128	0.125
323.15	0.135	0.132	0.129	0.125	0.122
333.15	0.133	0.130	0.127	0.123	0.119
343.15	0.131	0.128	0.125	0.120	0.117
353.15	0.129	0.127	0.122	0.118	0.114

^aRepeated from Chapter 4 for the reader's convenience.

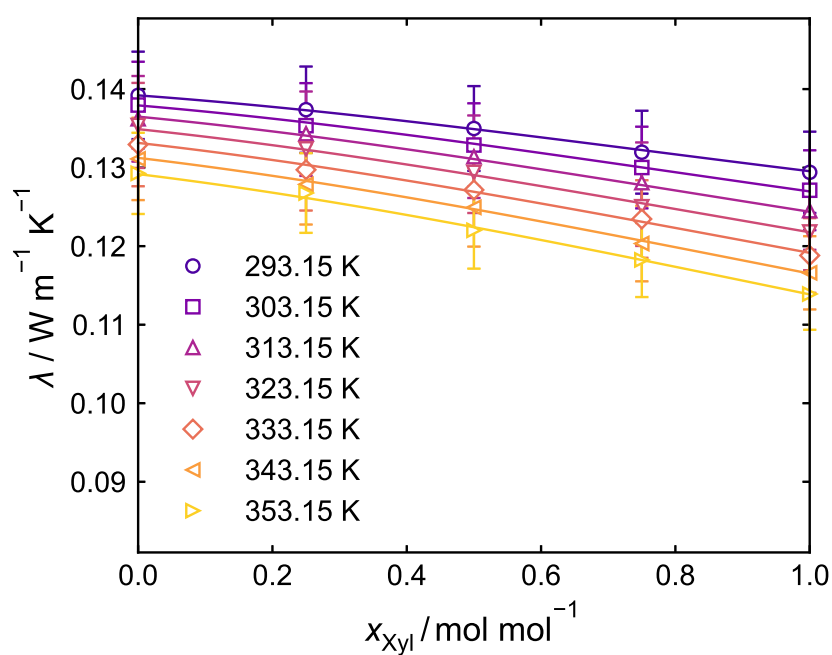


Figure 10: Thermal conductivity λ of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations (cf. Eqs. (5) – (7)) with parameters listed in Tables 21 and 22.

5.5 Isobaric Heat Capacity

Table 17 lists the experimental results for the isobaric heat capacity. They are shown in Figure 11 together with the correlation results. In agreement with expectations and previous results (see Ref. 36 and Chapter 4), the isobaric heat capacity decreases almost perfectly linearly with increasing *p*-xylene mole fraction. Its temperature dependence is different from that of the other properties discussed so far: the isobaric heat capacity increases with increasing temperature.

Table 17: Isobaric heat capacity c_p , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the isobaric heat capacity is $U_{\text{rel}}(c_p) = 0.06$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$c_p / \text{J mol}^{-1} \text{K}^{-1}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0 ^a	0.25	0.5	0.75	1
293.15	256	239	221	203	186
303.15	261	242	224	206	189
313.15	265	247	228	209	190
323.15	271	251	231	211	192
333.15	274	253	234	214	194
343.15	278	257	237	216	196
353.15	283	263	239	219	198

^aRepeated from Chapter 4 for the reader's convenience.

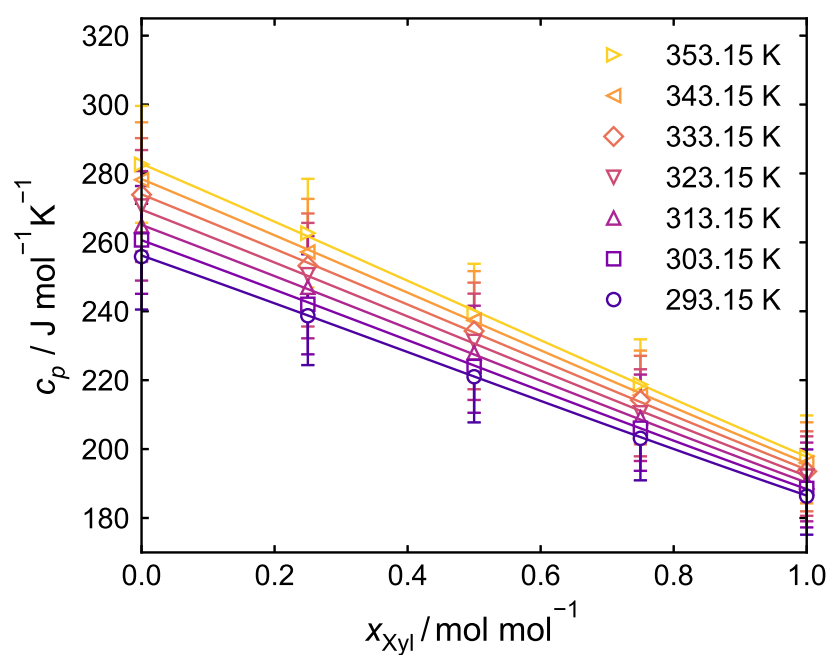


Figure 11: Isobaric heat capacity c_p of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations (cf. Eqs. (5) – (7)) with parameters listed in Tables 21 and 22.

5.6 Self-Diffusion Coefficients

Table 18 and Table 19 list the experimental results for the self-diffusion coefficients of EHA and *p*-xylene, respectively. They are shown in Figure 12 together with the correlation results. EHA is a larger molecule than *p*-xylene. Therefore, as expected, the self-diffusion coefficient of EHA is always lower than that of *p*-xylene at the same temperature and composition. Both self-diffusion coefficients increase with increasing temperature and increasing *p*-xylene mole fraction.

Table 18: Self-diffusion coefficient D_{EHA} , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{EHA}})$ ($k = 2$) are given in the table and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

		$D_{\text{EHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1} (U(D_{\text{EHA}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1})$				
		$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
T / K	0 ^a	0.02	0.25	0.50	0.75	0.95
298.15	0.127 (0.001)	0.136 (0.001)	0.246 (0.002)	0.429 (0.002)	0.664 (0.003)	0.970 (0.007)
313.15	0.214 (0.001)	0.229 (0.002)	0.372 (0.002)	0.596 (0.004)	0.887 (0.004)	1.178 (0.015)
333.15	0.375 (0.001)	0.395 (0.002)	0.569 (0.004)	0.835 (0.004)	1.191 (0.011)	1.590 (0.016)

^aRepeated from Chapter 4 for the reader's convenience.

Table 19: Self-diffusion coefficient D_{Xyl} , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{Xyl}})$ ($k = 2$) are given in the table and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

		$D_{\text{Xyl}} / 10^{-9} \text{ m}^2 \text{ s}^{-1} (U(D_{\text{Xyl}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1})$				
		$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
T / K	0.02	0.25	0.50	0.75	0.95	1
298.15	0.305 (0.022)	0.676 (0.006)	1.069 (0.004)	1.522 (0.003)	2.002 (0.003)	2.109 (0.004)
313.15	0.502 (0.024)	0.956 (0.013)	1.435 (0.004)	1.964 (0.005)	2.467 (0.004)	2.602 (0.005)
333.15	0.773 (0.044)	1.313 (0.040)	1.897 (0.014)	2.561 (0.013)	3.188 (0.014)	3.354 (0.025)

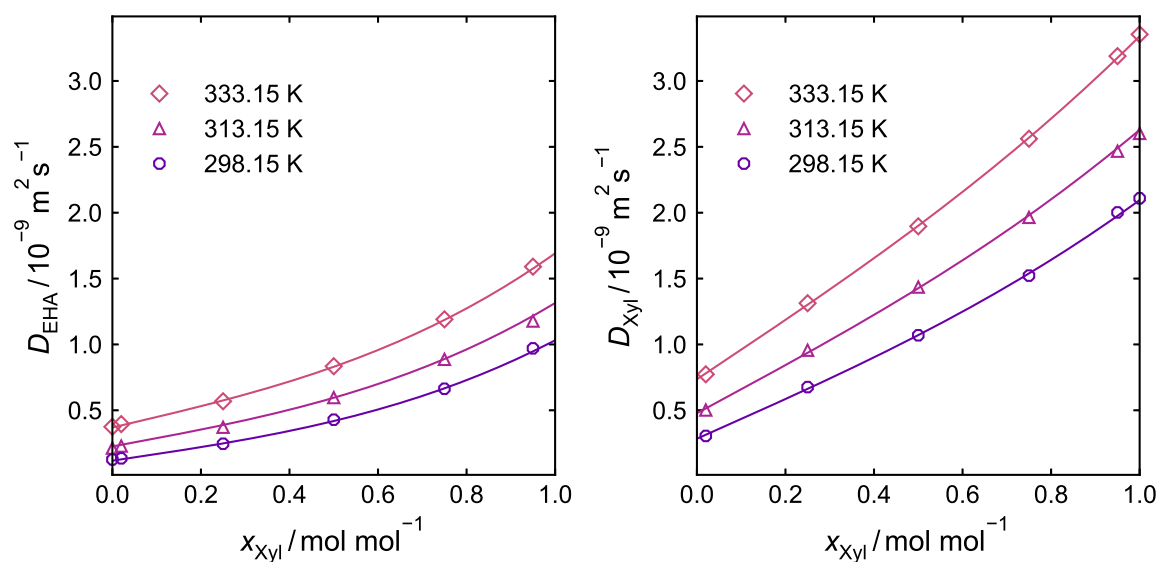


Figure 12: Self-diffusion coefficients of EHA D_{EHA} (left) and *p*-xylene D_{Xyl} (right) in mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations (cf. Eq. (12)) with parameters listed in Table 23.

5.7 Vapor-Liquid Equilibrium

Table 20 lists the results of the VLE measurements. They are shown in Figure 13 together with the model results. The VLE is wide-boiling and zeotropic. Although the NRTL model was only adapted to the pressure, the gas phase composition is also excellently reproduced.

At high *p*-xylene mole fractions, the activity coefficient of EHA (not shown) sharply increases and reaches high values. This is typical for an associating compound like EHA in a non-associating solvent like *p*-xylene. [89]

Table 20: Results of the isobaric VLE measurements: pressure p , temperature T , liquid phase mole fraction x_{Xyl} , and vapor phase mole fraction y_{Xyl} . The standard uncertainties are $u(p) = 0.1$ kPa, $u(T) = 0.1$ K, $u(x_{\text{Xyl}}) = u(y_{\text{Xyl}}) = 0.01$ mol mol⁻¹.

p / kPa	T / K	x_{Xyl} / mol mol ⁻¹	y_{Xyl} / mol mol ⁻¹
10	404.9	0.063	0.701
	382.1	0.166	0.932
	373.2	0.236	0.966
	367.2	0.284	0.978
	362.2	0.356	0.984
	346.4	0.720	0.996
	344.3	0.796	0.995
	342.4	0.901	0.995
20	409.9	0.136	0.821
	395.9	0.189	0.903
	394.1	0.209	0.916
	391.5	0.239	0.933
	385.1	0.314	0.970
	377.1	0.425	0.981
	374.1	0.498	0.985
	370.1	0.579	0.989
	369.9	0.563	0.984
	369.5	0.546	0.983
	366.8	0.987	0.987
	365.3	0.704	0.990
	365.3	0.702	0.990
	361.3	0.825	0.993
	359.3	0.959	0.994

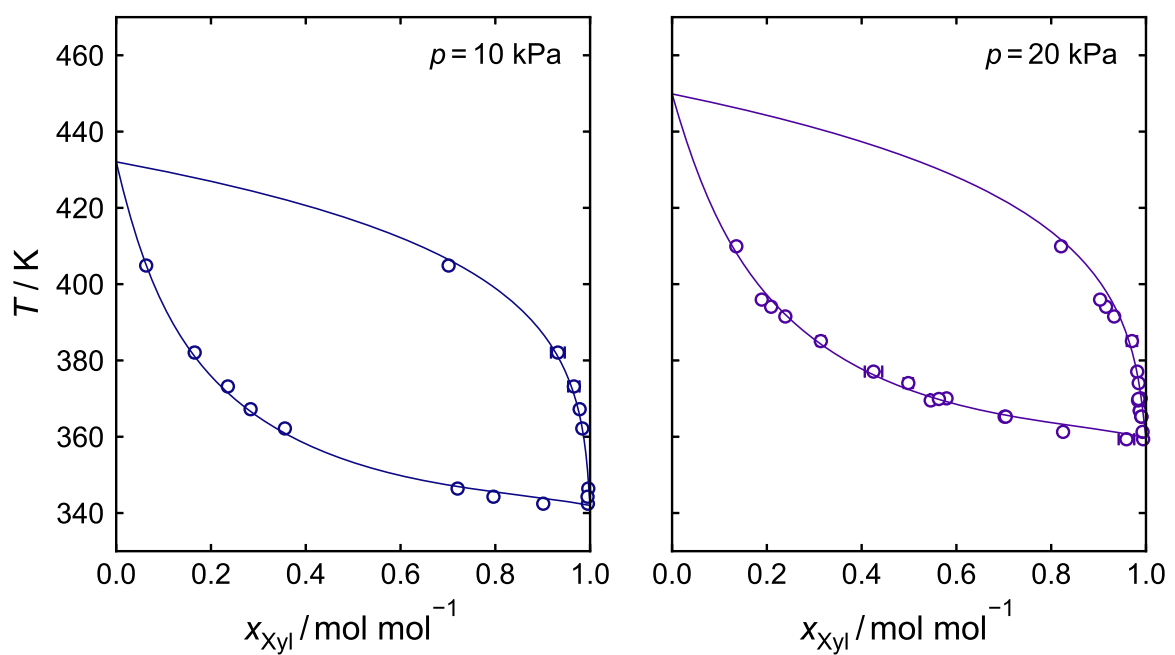


Figure 13: VLE of mixtures of EHA and *p*-xylene. Symbols are experimental results. Error bars indicate the experimental standard uncertainty. Lines show modeling results using the extended Raoult's law and the NRTL model for the activity coefficients (cf. Eqs. (18) – (22)) with parameters listed in Tables 24 and 25.

5.8 Lewis Number

Figure 14 shows the Lewis number of mixtures of EHA and *p*-xylene as a function of composition at different temperatures. The Lewis number decreases with increasing temperature. It is highest for high concentrations of EHA, reaches a local minimum at around $x_{\text{Xyl}} = 0.8 \text{ mol mol}^{-1}$, and increases slightly again for higher *p*-xylene mole fractions. The Lewis number is overall very high with values between 20 and almost 400, indicating that the heat transport is much faster than the diffusive mass transport in mixtures of EHA and *p*-xylene.

Due to the relatively slow mass transport and the wide-boiling VLE, EHA will tend to accumulate at the droplet surface during droplet evaporation. If the temperature continues to rise throughout the droplet, as promoted by the comparatively fast heat transfer, superheating can occur in the droplet interior, as shown for mixtures of TTIP and *p*-xylene in Chapter 8. Eventually, this superheating can lead to droplet micro-explosions. This agrees with the fact that micro-explosions have been observed in single droplet combustion experiments with mixtures of EHA and *p*-xylene.[86]

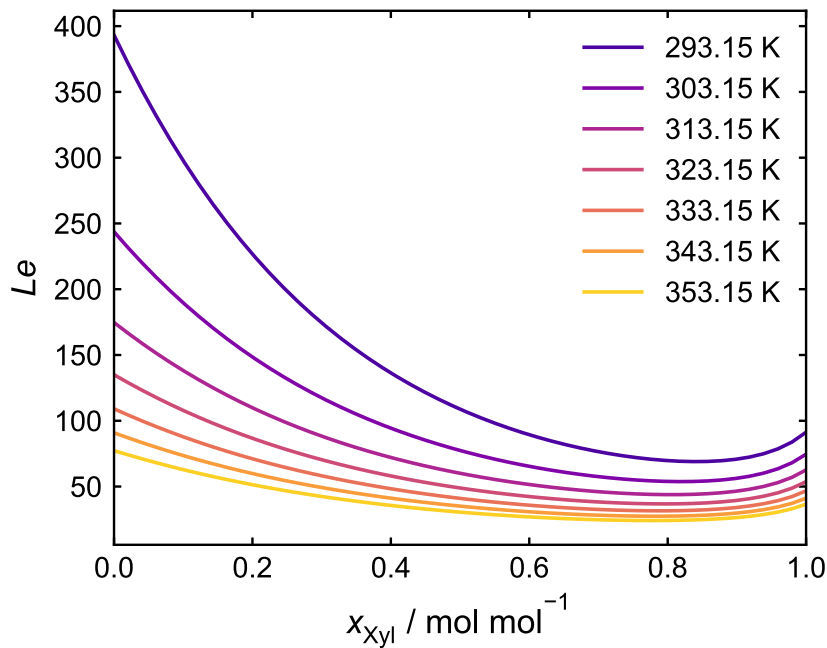


Figure 14: Lewis number Le of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures.

5.9 Parameters

The parameters of the correlations for the pure component molar volumes, viscosities, thermal conductivities, and isobaric heat capacities of EHA and *p*-xylene are given in Table 21. The parameters of the correlations for the excess molar volumes, viscosities, thermal conductivities, and isobaric heat capacities of mixtures of EHA and *p*-xylene are given in Table 22. The parameters of the correlations for the self-diffusion coefficients of EHA and *p*-xylene in mixtures of EHA and *p*-xylene are given in Table 23. The parameters of the Antoine-type equation used for the vapor pressures of pure EHA and pure *p*-xylene are repeated from Chapter 4 and Ref. 36 in Table 24. The parameters of the NRTL model for the calculation of the activity coefficients are given in Table 25.

Table 21: Parameters of the correlations for the pure-component properties of EHA^a and *p*-xylene.

property z	Eq.	$a_{i,z}$	$b_{i,z}$	$c_{i,z}$
$v_{\text{EHA}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	1.1481×10^{-4}	1.5090×10^{-7}	0 ^b
$\eta_{\text{EHA}}^{\text{pure}} / \text{mPa s}$	(11)	7.4089×10^{-5}	3.3525×10^3	6.6045×10^{-1}
$\lambda_{\text{EHA}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	1.0638×10^{-1}	3.4356×10^{-4}	-7.9010×10^{-7}
$c_{p,\text{EHA}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	1.2608×10^2	4.4382×10^{-1}	0 ^b
$v_{\text{Xyl}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	8.3752×10^{-5}	1.3460×10^{-7}	0 ^b
$\eta_{\text{Xyl}}^{\text{pure}} / \text{mPa s}$	(11)	4.2349×10^{-3}	1.4209×10^3	1.2468×10^{-1}
$\lambda_{\text{Xyl}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	1.9795×10^{-1}	-2.1000×10^{-4}	-7.9645×10^{-8}
$c_{p,\text{Xyl}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	1.3144×10^2	1.8782×10^{-1}	0 ^b

^aRepeated from Chapter 4 for the reader's convenience.

^bNot needed and set to zero.

Table 22: Parameters of the correlations for the excess properties of mixtures of EHA and *p*-xylene.

property z	Eq.	E_z	F_z	G_z
$v / \text{m}^3 \text{ mol}^{-1}$	(7)	-1.0615×10^{-6}	2.1219×10^{-9}	-9.2538×10^{-9}
$\eta / \text{mPa s}$	(10)	-1.9665×10^2	-2.5993×10^1	0 ^a
$\lambda / \text{W m}^{-1} \text{ K}^{-1}$	(7)	-5.0315×10^{-3}	2.4421×10^{-5}	-1.3071×10^{-3}
$c_p / \text{J mol}^{-1} \text{ K}^{-1}$	(7)	-5.2968	1.4227×10^{-2}	-2.4412

^aNot needed and set to zero.

Table 23: Parameters of the correlations for the self-diffusion coefficients of EHA and *p*-xylene in mixtures of EHA and *p*-xylene (see Eq. (12)).

property	a_{i,D_i}	b_{i,D_i}	c_{i,D_i}	d_{i,D_i}	e_{i,D_i}	f_{i,D_i}
$D_{\text{EHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$	-2.026	7.191×10^{-3}	-1.974	8.290×10^{-3}	-5.905×10^{-1}	3.377×10^{-3}
$D_{\text{Xyl}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$	-3.560	1.289×10^{-2}	-4.861	2.131×10^{-2}	-7.765×10^{-2}	1.327×10^{-3}

Table 24: Antoine parameters for EHA and *p*-xylene obtained previously (see Chapter 4 and Ref. 36) from fits of Eq. (19) to the indicated literature data.

component	A_i	B_i	C_i	Ref.
EHA	15.2351	-4066.6	-117.614	71
<i>p</i> -xylene	14.0775	-3344.9	-57.910	90

Table 25: NRTL parameters obtained from a fit to the present experimental VLE data (see Eqs. (23) and (22)).

α	$\tau_{\text{EHA,Xyl}}$	$\tau_{\text{Xyl,EHA}}$
0.3	-0.8640	2.3013

6 Thermophysical Properties of Mixtures of (SnEHA + *p*-Xylene)

6.1 State of the Art

SnEHA is most commonly used as a catalyst for polymerization reactions, e.g., for the synthesis of polylactic acid. [91–93] Furthermore, it can be used as an organometallic precursor for producing tin-based nanoparticles via spray flame synthesis. [3–5, 20, 21, 94–96] Formally, SnEHA is the tin(II) salt of EHA. However, research indicates that it actually exists as a coordination complex [92, 97], analogous to, for example, copper(II) hexanoate [98] and zinc carboxylates [99]. SnEHA is liquid at ambient conditions. It can undergo (partial) hydrolysis, which releases EHA [34, 92] to eventually form tin oxide. The pure component properties of SnEHA are mostly unknown.

In spray flame synthesis applications, SnEHA is usually used with xylene [3, 20, 21] or mixtures of xylene and acetonitrile [4, 5, 94–96] as solvents. The produced tin oxide (SnO₂) is frequently applied to make gas sensors [3–5, 20, 21, 94–96, 100, 101].

Aside from particle production for gas sensing applications, precursor solutions made of SnEHA and xylene are employed in fundamental studies in the field of spray flame synthesis. They have been used in single droplet combustion experiments, confirming the occurrence of micro-explosions during droplet evaporation and combustion. [87] Additionally, in these single droplet combustion experiments, the droplets were studied with interferometric particle imaging and standard rainbow refractometry to gain insights into heat and mass transfer processes inside the droplets. [27]

6.2 Density

The results of the density measurements are reported in Table 26 and depicted in Figure 15. Unsurprisingly, the density decreases with increasing temperature. Pure SnEHA has a significantly higher density than pure *p*-xylene; thus, the density decreases with increasing *p*-xylene mole fraction. The molar volume (not shown) of mixtures of SnEHA and *p*-xylene depends almost linearly on the *p*-xylene mole fraction, indicating a near-ideal mixture behavior for this property.

Table 26: Density ρ , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainty of the density is $U(\rho) = 1 \text{ kg m}^{-3}$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), and $u(p) = 3 \text{ kPa}$ and $u(T) = 0.05 \text{ K}$.

T / K	$\rho / \text{kg m}^{-3}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1 ^a
293.15	1302.9	1251.8	1174.2	1064.8	861.1
303.15	1293.9	1242.3	1164.6	1055.4	852.4
313.15	1283.9	1232.9	1154.9	1045.9	843.5
323.15	1274.1	1223.2	1145.3	1036.4	834.9
333.15	1263.9	1213.5	1135.3	1027.0	826.0
343.15	1255.5	1203.6	1125.6	1017.4	817.1
353.15	1245.7	1193.4	1115.9	1007.9	808.1

^aRepeated from Chapter 5 for the reader's convenience.

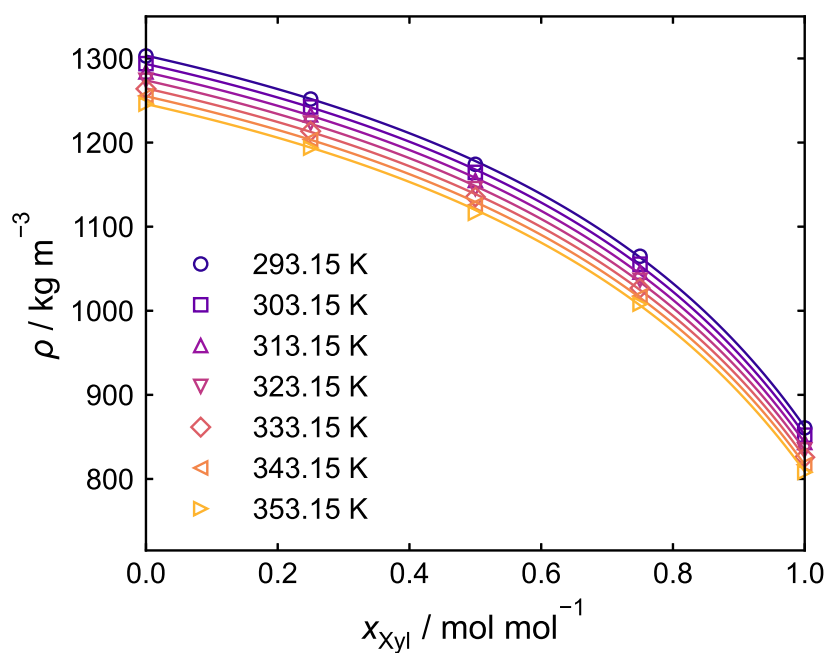


Figure 15: Density ρ of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations, cf. Eqs. (5) – (9), with parameters listed in Tables 32 and 33.

6.3 Viscosity

The results of the viscosity measurements are reported in Table 27 and depicted in Figure 16. Unsurprisingly, the viscosity decreases with increasing temperature. Pure SnEHA has an extremely high viscosity, especially compared to that of pure *p*-xylene, and thus, the viscosity decreases exponentially with increasing *p*-xylene mole fraction. The values of the mixture viscosity span several orders of magnitude. Overall, however, the chosen Jouyban-Acree model is able to describe this behavior well, showing the largest deviations between the experimental results and the correlation at $x_{\text{Xyl}} = 0.75$ mol mol⁻¹.

Table 27: Viscosity η , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the viscosity $U(\eta)$ ($k = 2$) are given in the table, and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.05$ K.

T / K	$\eta / \text{mPa s } (U(\eta) / \text{mPa s})$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1 ^b
293.15	3756 (35.2)	415.2 (4.347)	34.50 (0.314)	3.063 (0.048)	0.664 (0.006)
303.15	1391 (11.88)	184.4 (3.597)	19.12 (0.182)	2.451 (0.021)	0.587 (0.005)
313.15	559.7 (4.814)	92.97 (1.163)	11.38 (0.105)	2.001 (0.017)	0.515 (0.009)
323.15	252.2 (2.611)	48.29 (0.624)	7.323 (0.062)	1.669 (0.014)	0.471 (0.005)
333.15	113.6 (4.941)	24.70 (0.569)	5.188 (0.044)	1.420 (0.012)	0.427 (0.004)
343.15	69.09 (1.046)	16.84 (0.215)	3.886 (0.034)	1.226 (0.01)	0.391 (0.004)
353.15	38.52 (0.341)	10.72 (0.132)	3.049 (0.026)	1.076 (0.009)	0.360 (0.004)

^aRepeated from Chapter 5 for the reader's convenience.

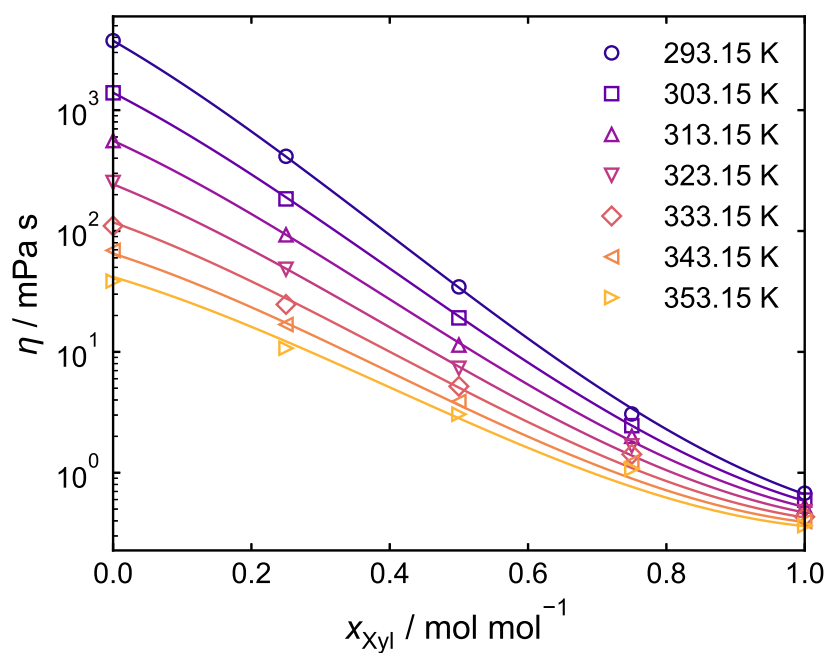


Figure 16: Viscosity η of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations, cf. Eqs. (10) and (11), with parameters listed in Tables 32 and 33.

6.4 Thermal Conductivity

The results of the thermal conductivity measurements are reported in Table 28 and depicted in Figure 17. Like in most previously investigated mixtures of relevance to spray flame synthesis, see Refs. 36, 39 and Chapters 4 and 5, the thermal conductivity decreases with increasing temperature. The thermal conductivity of pure SnEHA is slightly higher than that of pure *p*-xylene, and therefore, the mixture thermal conductivity decreases with increasing *p*-xylene mole fraction.

Table 28: Thermal conductivity λ , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the thermal conductivity is $U_{\text{rel}}(\lambda) = 0.04$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$\lambda / \text{W m}^{-1} \text{K}^{-1}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1 ^b
293.15	0.144	0.141	0.138	0.134	0.129
303.15	0.142	0.139	0.137	0.131	0.127
313.15	0.142	0.137	0.135	0.129	0.125
323.15	0.140	0.136	0.132	0.127	0.122
333.15	0.137	0.133	0.130	0.125	0.119
343.15	0.135	0.131	0.128	0.123	0.117
353.15	0.133	0.130	0.126	0.121	0.114

^aRepeated from Chapter 5 for the reader's convenience.

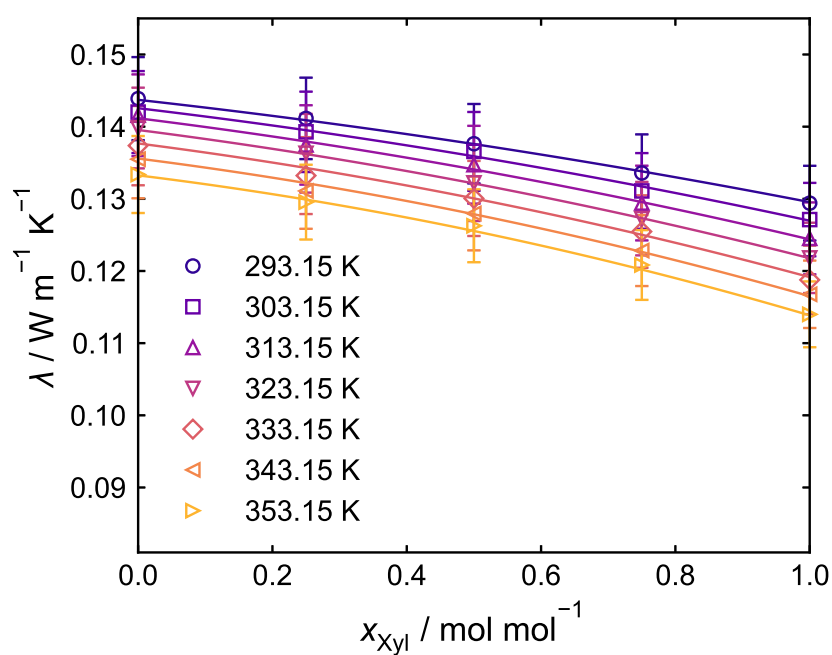


Figure 17: Thermal conductivity λ of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations, cf. Eqs. (5) – (7), with parameters listed in Tables 32 and 33.

6.5 Isobaric Heat Capacity

The results of the isobaric heat capacity measurements are reported in Table 29 and depicted in Figure 18. Like in previously investigated mixtures, see Refs. 36–39 and Chapters 4 and 5, the isobaric heat capacity increases with increasing temperature. In connection to the large molecular mass of SnEHA, the molar isobaric heat capacity of pure SnEHA is higher than that of pure *p*-xylene. The isobaric heat capacity decreases almost perfectly linearly with increasing *p*-xylene mole fraction.

Table 29: Isobaric heat capacity c_p , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded relative uncertainty of the isobaric heat capacity is $U_{\text{rel}}(c_p) = 0.06$ ($k = 2$), and $U(x_{\text{Xyl}}) = 0.001$ mol mol^{−1} ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$c_p / \text{J mol}^{-1} \text{K}^{-1}$				
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$				
	0	0.25	0.5	0.75	1 ^b
293.15	514	429	347	264	186
303.15	521	435	353	266	189
313.15	533	441	358	271	190
323.15	541	450	362	274	192
333.15	547	452	367	278	194
343.15	554	458	371	281	196
353.15	561	466	377	285	198

^aRepeated from Chapter 5 for the reader's convenience.

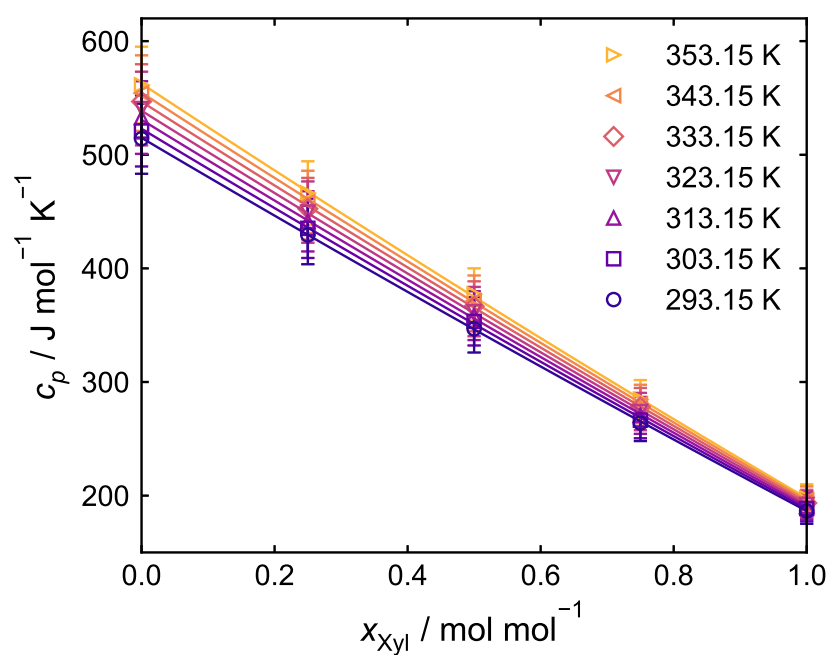


Figure 18: Isobaric heat capacity c_p of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Error bars indicate the combined expanded uncertainty. Lines are empirical correlations, cf. Eqs. (5) – (7), with parameters listed in Tables 32 and 33.

6.6 Self-Diffusion Coefficients

The relative combined expanded uncertainty of the self-diffusion coefficient D_i of component i is usually about $U_{\text{rel}}(D_i) = 0.02$ ($k = 2$) [40]. However, this uncertainty varies depending on the temperature and the sample composition. For the self-diffusion coefficient of *p*-xylene, it is specified together with the measurement results. The self-diffusion coefficient of SnEHA is extremely low. Moreover, especially at low temperatures and high SnEHA contents, the high viscosity decreases the relaxation time of the nuclei, which increases the line width in the spectra [102], and thereby could contribute to measurement errors. Hence, the combined expanded uncertainty of the self-diffusion coefficient of SnEHA is conservatively estimated to be at least $U(D_{\text{SnEHA}}) = 0.002 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ($k = 2$). Consequently, the uncertainty reported together with the results for D_{SnEHA} is either $U_{\text{rel}}(D_i) = 0.02$ or $U(D_{\text{SnEHA}}) = 0.002 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, whichever is larger.

The results of the measurements of the self-diffusion coefficient of SnEHA are reported in Table 30. The results of the measurements of the self-diffusion coefficient of *p*-xylene are reported in Table 31. The self-diffusion coefficients are depicted in Figure 19. As anticipated for a highly viscous fluid with a high molar mass, the self-diffusion coefficient of SnEHA is extremely low at high SnEHA concentrations, especially at low temperatures. Likewise, the self-diffusion coefficient of *p*-xylene is low at high SnEHA concentrations, especially at low temperatures. As for the viscosity, the values of the self-diffusion coefficients span several orders of magnitude. The self-diffusion coefficients of both components increase strongly with increasing temperature and increasing *p*-xylene mole fraction. Overall, the proposed correlation represents the data well. The largest deviations between the experimental data and the correlation for D_{SnEHA} occur at $x_{\text{Xyl}} = 0.75 \text{ mol mol}^{-1}$.

Table 30: Self-diffusion coefficient D_{SnEHA} , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3 \text{ kPa}$. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{SnEHA}})$ ($k = 2$) are given in the table, and $U(x_{\text{Xyl}}) = 0.001 \text{ mol mol}^{-1}$ ($k = 2$), $u(p) = 3 \text{ kPa}$, and $u(T) = 0.1 \text{ K}$.

T / K	$D_{\text{SnEHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ } (U(D_{\text{SnEHA}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1})$		
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$		
	0	0.25	0.75
298.15		0.003 (0.002)	0.091 (0.002)
313.15	0.002 (0.002)	0.007 (0.002)	0.149 (0.003)
333.15	0.007 (0.002)	0.019 (0.002)	0.245 (0.005)
353.15	0.014 (0.002)	0.043 (0.002)	0.974 (0.019)

Table 31: Self-diffusion coefficient D_{Xyl} , liquid mole fraction x_{Xyl} , and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{Xyl}})$ ($k = 2$) are given in the table, and $U(x_{\text{Xyl}}) = 0.001$ mol mol⁻¹ ($k = 2$), $u(p) = 3$ kPa, and $u(T) = 0.1$ K.

T / K	$D_{\text{Xyl}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ($U(D_{\text{Xyl}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1}$)			
	$x_{\text{Xyl}} / \text{mol mol}^{-1}$			
	0.25	0.5	0.75	1
298.15	0.043 (0.001)	0.048 (0.002)	0.440 (0.008)	2.109 (0.004) ^a
313.15	0.100 (0.002)	0.106 (0.002)	0.519 (0.018)	2.602 (0.005) ^a
333.15	0.226 (0.001)	0.236 (0.002)	0.952 (0.024)	3.354 (0.025) ^a
353.15	0.419 (0.003)	0.503 (0.010)	1.230 (0.028)	4.220 (0.084)

^aRepeated from Chapter 5 for the reader's convenience.

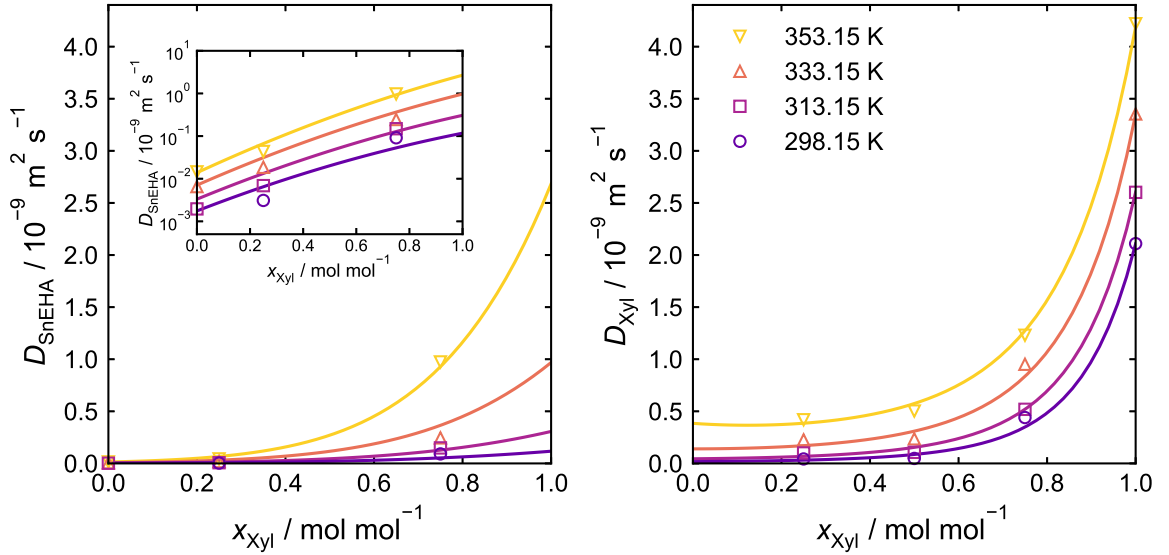


Figure 19: Self-diffusion coefficient of SnEHA D_{SnEHA} (left) and p -xylene D_{Xyl} (right) in mixtures of SnEHA and p -xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. The inset in the left panel shows the same data as the main plot, but logarithmically. In the inset, the uncertainties are not shown for better clarity. Lines are empirical correlations, cf. Eq. (13), with parameters listed in Table 34.

6.7 Lewis Number

Due to the lack of VLE data for evaluating the activity coefficients, and consequently, for calculating the thermodynamic factor to obtain Fickian diffusion coefficients, the Lewis number is defined here using the Maxwell-Stefan diffusion coefficient of the system, i.e.:

$$Le = \frac{a}{D} \quad (27)$$

The results for the Lewis number are depicted in Figure 20. The Lewis number is very high at all investigated temperatures and over the entire composition range, which indicates that the diffusive mass transfer is orders of magnitude slower than the heat transfer. This is likely to contribute to the occurrence of superheating and, thereby, micro-explosions (see Chapter 8) when mixtures of SnEHA and *p*-xylene are used as precursor solutions for the spray flame synthesis of nanoparticles. This is consistent with the observation of micro-explosions in single droplet combustion experiments with this material system. [27, 87]

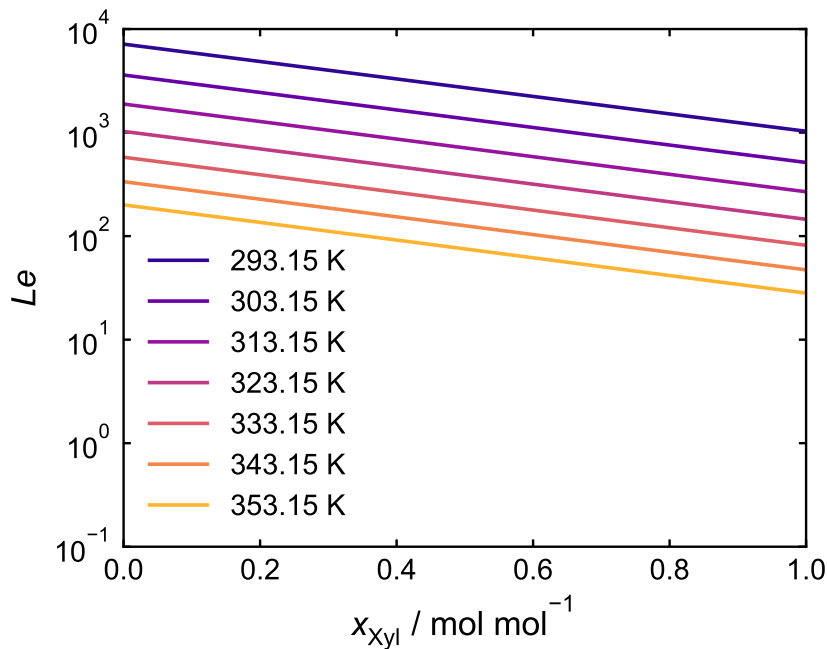


Figure 20: Lewis number Le in mixtures of SnEHA and *p*-xylene at different temperatures.

6.8 Parameters

The parameters of the pure component property correlations (Eqs. (6) and (11)) are listed in Table 32. The parameters for pure *p*-xylene are the same as in Chapter 5 and are repeated here for the reader's convenience. The parameters of the excess property correlations for the molar volume, the thermal conductivity, and the isobaric heat capacity (Eq. (5)) and the Jouyban-Acree correlation for the viscosity (Eq. (10)) are listed in Table 33. The parameters of the correlation for the self-diffusion coefficients of SnEHA and *p*-xylene are listed in Table 34.

Table 32: Parameters of the correlations for the pure-component properties of SnEHA and *p*-xylene^a.

property z	Eq.	$a_{i,z}$	$b_{i,z}$	$c_{i,z}$
$v_{\text{SnEHA}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	2.4076×10^{-4}	2.3897×10^{-7}	0^{b}
$\eta_{\text{SnEHA}}^{\text{pure}} / \text{mPa s}$	(11)	2.4904×10^{-10}	8.8938×10^3	2.1068×10^{-1}
$\lambda_{\text{SnEHA}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	7.3711×10^{-2}	5.8180×10^{-4}	-1.1700×10^{-6}
$c_{p,\text{SnEHA}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	2.8204×10^2	7.9431×10^{-1}	0^{b}
$v_{\text{Xyl}}^{\text{pure}} / \text{m}^3 \text{ mol}^{-1}$	(6)	8.3752×10^{-5}	1.3460×10^{-7}	0^{b}
$\eta_{\text{Xyl}}^{\text{pure}} / \text{mPa s}$	(11)	4.2349×10^{-3}	1.4209×10^3	1.2468×10^{-1}
$\lambda_{\text{Xyl}}^{\text{pure}} / \text{W m}^{-1} \text{ K}^{-1}$	(6)	1.9795×10^{-1}	-2.1000×10^{-4}	-7.9645×10^{-8}
$c_{p,\text{Xyl}}^{\text{pure}} / \text{J mol}^{-1} \text{ K}^{-1}$	(6)	1.3144×10^2	1.8782×10^{-1}	0^{b}

^aRepeated from Chapter 5 for the reader's convenience.

^bNot needed and set to zero.

Table 33: Parameters of the correlations for the excess properties of mixtures of SnEHA and *p*-xylene.

property z	Eq.	E_z	F_z	G_z
$v / \text{m}^3 \text{ mol}^{-1}$	(7)	0^{a}	0^{a}	0^{a}
$\eta / \text{mPa s}$	(10)	-4.4985×10^2	-7.4563×10^2	0^{a}
$\lambda / \text{W m}^{-1} \text{ K}^{-1}$	(7)	-1.6334×10^{-2}	6.8795×10^{-5}	0^{a}
$c_p / \text{J mol}^{-1} \text{ K}^{-1}$	(7)	-3.0885×10^{-1}	-5.8581×10^{-2}	0^{a}

^aNot needed and set to zero.

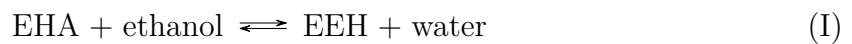
Table 34: Parameters of the correlation for the self-diffusion coefficient of SnEHA and *p*-xylene in mixtures of SnEHA and *p*-xylene (see Eq. (13)).

property	a_{i,D_i}	b_{i,D_i}	c_{i,D_i}	d_{i,D_i}	e_{i,D_i}
$D_{\text{SnEHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$	1000	13.2525	6.3296×10^7	20.1078	3.8998
$D_{\text{Xyl}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$	173.761	4.41208	8.2831×10^6	20	0.04196

7 Liquid-Liquid Equilibria in Mixtures of (EHA + Ethanol + Water)

7.1 State of the Art

For understanding and improving spray flame synthesis processes, the properties of the ternary system (EHA + ethanol + water) are relevant for several reasons. First, many typical precursor metal salts, such as iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), contain water bound in the crystal structure that is released in solution. [103] The solid-liquid equilibria and thermophysical properties of mixtures of iron nitrate nonahydrate with ethanol or 1-propanol were studied in Refs. 37, 38, 103. Second, water occurs as a product of the combustion reaction of the precursor solution. [104] Third, carboxylic acids such as EHA can undergo esterification reactions with alcohols such as ethanol to form esters (here: ethyl 2-ethylhexanoate, EEH) and water, see reaction (I).



If iron ions are present in the precursor solution, they act as a catalyst for this reaction. [22, 23] A preliminary study, the results of which are reported in Appendix D, confirmed that the extent of the esterification reaction between EHA and ethanol was negligible at room temperature.

The presence of water in the precursor solution is especially relevant because of its miscibility gap with EHA. [105] It is to be expected that the possible formation of a second liquid phase inside of the droplet has an impact on the evaporation and combustion process, and hence on the product properties. [26] However, investigating this requires information on LLE in the ternary system (EHA + ethanol + water). Only one tie line has been reported in the literature for the binary subsystem (EHA + water) [105] and there are no data for the ternary system. EHA and ethanol are fully miscible.

7.2 Liquid-Liquid Equilibria in the Binary System (EHA + Water)

The experimental results for the LLE in the binary subsystem (EHA + water) are listed in Table 35. Figure 21 depicts the mole fraction of EHA in the EHA-rich phase of the LLE in the binary system (EHA + water) for different temperatures, together with the results of the NRTL model. The EHA content of the water-rich phase was below the detection limit of $0.0005 \text{ mol mol}^{-1}$ and is, therefore, not shown. At 298 K, the data agree well with the single available data point from the literature [105]. The solubility of water in EHA increases with increasing temperature. The model correlates the experimental data well.

Table 35: LLE in the binary system (EHA + water) at atmospheric pressure $p = 101.3 \text{ kPa}$ and different temperatures T . The standard uncertainties are $u(T) = 0.1 \text{ K}$, $u(x) = 0.01 \text{ mol mol}^{-1}$, and $u(p) = 3 \text{ kPa}$.

T / K	$x'_{\text{EHA}} / \text{mol mol}^{-1}$	$x''_{\text{EHA}} / \text{mol mol}^{-1}$
283.2	0.921	0 ^a
293.2	0.910	
298.2	0.905	
303.3	0.908	
313.2	0.895	
323.5	0.890	
333.6	0.895	

^aThe experimental mole fraction of EHA in the water-rich phase was lower than the detection limit of $0.0005 \text{ mol mol}^{-1}$ in all experiments.

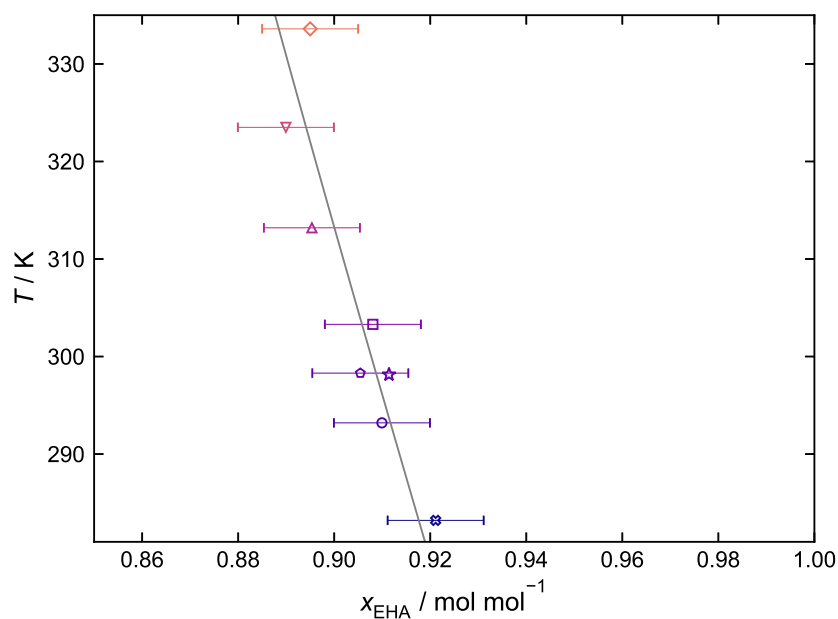


Figure 21: Mole fraction of EHA in the EHA-rich phase of the LLE in the binary system (EHA + water) at different temperatures. Symbols are experimental results. Error bars indicate the experimental uncertainty of the mole fraction of EHA. The uncertainty of the temperature measurement is within symbol size. The star symbol denotes the single available experimental data point from the literature [105]. The line denotes the model results. The experimental mole fraction of EHA in the water-rich phase is lower than the detection limit of $0.0005 \text{ mol mol}^{-1}$ and hence not depicted here.

7.3 Liquid-Liquid Equilibria in the Ternary System (EHA + Ethanol + Water)

The experimental results for the LLE in the ternary system (EHA + ethanol + water) are listed in Table 36. Figure 22 depicts the LLE in the ternary system (EHA + ethanol + water) at temperatures of 283.2, 293.2, 303.3, 313.2, 323.5, and 333.6 K. In all cases, the experimental feed compositions lie on the experimental tie lines, indicating the consistency of the results. The phase separation between EHA and water vanishes for ethanol mole fractions above approximately 0.35 mol mol⁻¹, hence ethanol acts as a solubilizer for EHA-water mixtures. Overall, the results for all temperatures are very similar. Consistent with the findings for the binary subsystem (EHA + water), the miscibility gap becomes slightly narrower with increasing temperature. Using the parameters adjusted to the ternary LLE data for the subsystem (ethanol + water), the model describes the experimental results well.

Table 36: Compositions of gravimetrically-prepared samples (superscript *Feed*) and compositions of the phases in equilibrium (superscripts ' and '') in the ternary system (EHA + ethanol + water) at atmospheric pressure $p = 101.3$ kPa and different temperatures T . The standard uncertainties are $u(T) = 0.1$ K, $u(x) = 0.01$ mol mol⁻¹, and $u(p) = 3$ kPa.

T / K	$x_{\text{EHA}}^{\text{Feed}}$ / mol mol ⁻¹	$x_{\text{EtOH}}^{\text{Feed}}$ / mol mol ⁻¹	x'_{EHA} / mol mol ⁻¹	x'_{EtOH} / mol mol ⁻¹	x''_{EHA} / mol mol ⁻¹	x''_{EtOH} / mol mol ⁻¹
283.2	0.400	0.041	0.831	0.044	0 ^a	0.019
	0.340	0.080	0.717	0.112	0.001	0.041
	0.285	0.120	0.603	0.179	0 ^a	0.054
	0.240	0.160	0.492	0.241	0.001	0.075
	0.080	0.295	0.128	0.364	0.004	0.171
293.2	0.400	0.041	0.810	0.046	0 ^a	0.017
	0.340	0.080	0.696	0.117	0 ^a	0.034
	0.285	0.120	0.585	0.179	0.001	0.052
	0.240	0.160	0.478	0.239	0.001	0.069
	0.136	0.242	0.255	0.349	0.001	0.112
303.3	0.080	0.295	0.112	0.346	0.006	0.172
	0.400	0.041	0.806	0.050	0 ^a	0.015
	0.340	0.080	0.694	0.114	0 ^a	0.030
	0.285	0.120	0.583	0.177	0.001	0.047
	0.240	0.160	0.476	0.238	0.001	0.065
313.2	0.190	0.200	0.376	0.293	0.001	0.082
	0.136	0.242	0.249	0.348	0.001	0.108
	0.400	0.041	0.797	0.048	0 ^a	0.013
	0.340	0.080	0.681	0.113	0 ^a	0.031
	0.285	0.120	0.582	0.175	0 ^a	0.041
323.5	0.240	0.160	0.470	0.241	0 ^a	0.059
	0.080	0.295	0.100	0.315	0.005	0.162
	0.400	0.041	0.791	0.050	0 ^a	0.012
	0.285	0.120	0.567	0.179	0 ^a	0.041
	0.240	0.160	0.472	0.233	0.001	0.054
333.6	0.190	0.200	0.358	0.295	0.001	0.077
	0.136	0.242	0.253	0.336	0.001	0.103
	0.080	0.295	0.098	0.315	0.006	0.163
	0.400	0.041	0.797	0.047	0 ^a	0.012
	0.340	0.080	0.679	0.116	0 ^a	0.025
	0.285	0.120	0.573	0.179	0 ^a	0.039
	0.240	0.160	0.471	0.238	0.001	0.055
	0.190	0.200	0.363	0.295	0.001	0.072
	0.136	0.242	0.253	0.341	0.001	0.100
	0.080	0.295	0.105	0.325	0.006	0.158

^aThe experimental mole fraction of EHA in the water-rich phase was lower than the detection limit of 0.0005 mol mol⁻¹.

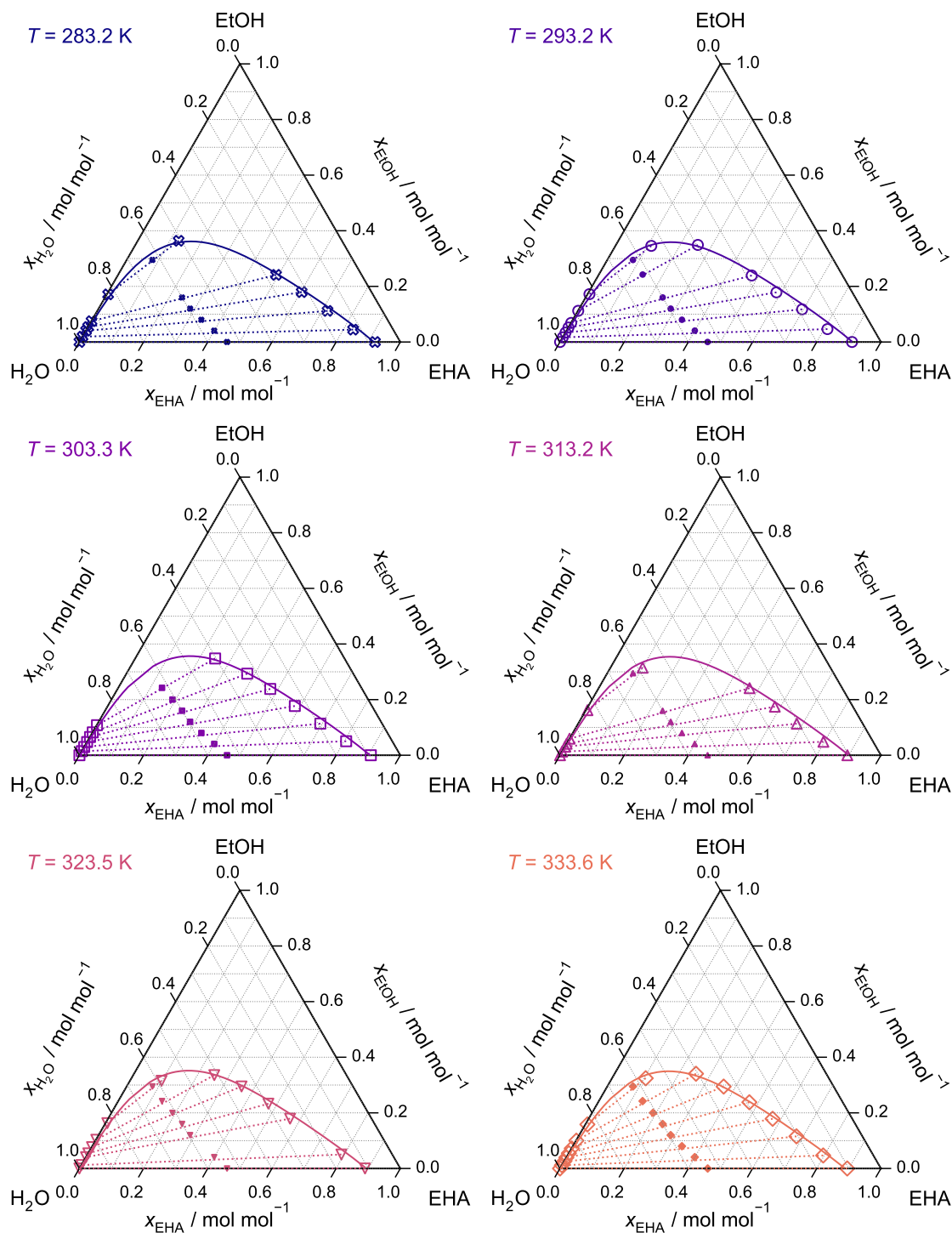


Figure 22: LLE in the system (EHA + ethanol + water) at different temperatures. Open symbols are experimental results for the equilibrium phase compositions of the LLE. Filled symbols are feed compositions. Dotted lines are experimental tie lines. Solid lines are model results using the parameters adapted to the ternary LLE for the subsystem (ethanol + water), see Section 7.5. Error bars are within symbol size.

7.4 Residue Curves

In order to estimate whether liquid-liquid demixing is likely to occur during droplet evaporation, residue curves were calculated. Residue curves are calculated by solving the differential equation for the change of the liquid composition during single-stage batch distillation. [106] The concept includes the assumption of an ideally mixed liquid phase, and here, additionally, the gas phase is assumed to be ideal (see Eq. (18)). For the residue curve calculation, the NRTL parameters in the binary subsystem (ethanol + water) that were adjusted to the binary VLE in that subsystem were used (see Section 7.5). During the evaporation of a real spray flame droplet, noncondensable gases are present in the gas phase. Since their solubility in the liquid phase can be assumed to be very low, they can be neglected in the residue curve calculation as they do not change the VLE other than increasing the total pressure.

Figure 23 depicts the residue curves of the system (EHA + ethanol + water) at 1 bar calculated using *Aspen Plus V12*. Also, the LLE at an exemplary temperature of 400 K (calculated with the parameters adjusted to the ternary LLE data, see Section 7.5) as well as typical initial compositions of solvent mixtures used in spray flame synthesis [24, 107, 108] are shown. The residue curves that go through these points never come close to the LLE envelope, which means that a liquid-liquid split will probably not occur. However, as shown Chapter 8, the evaporation of a spray flame droplet is highly influenced by the coupled heat and mass transfer inside the droplet, which might alter this finding. The influence of these transport phenomena is a topic for future exploration, which falls outside of the scope of the present study.

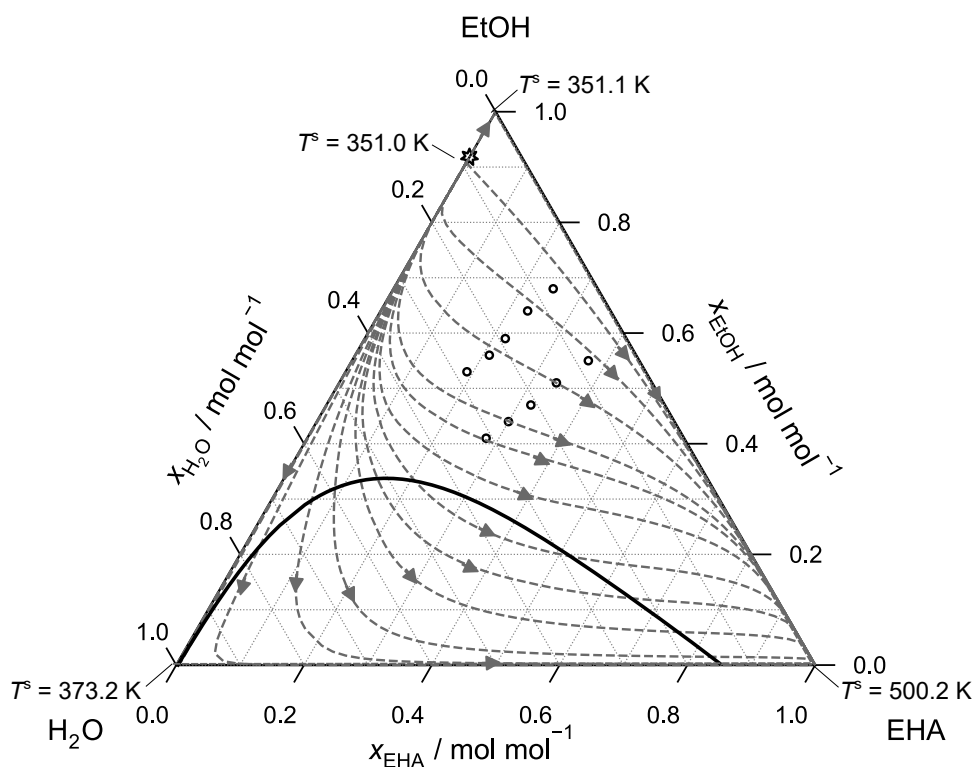


Figure 23: Residue curves in the ternary system (EHA + ethanol + water) at 1 bar. The dashed lines denote residue curves, which were calculated with the parameters of the system (ethanol + water) that were adjusted to VLE data in that system, see Section 7.5. The star denotes the position of the binary low-boiling azeotrope in the subsystem (ethanol + water). The small circles indicate the initial compositions of typical solvent mixtures relevant for spray flame synthesis processes [24, 107, 108]. The solid line shows the LLE model results at 400 K, evaluated with the parameters of the system (ethanol + water) that were adjusted to the ternary LLE data, see Section 7.5. The shown values for T^s indicate the boiling temperatures of the pure components and the azeotrope at 1 bar.

7.5 Parameters

The parameters for the Antoine equation are reported in Table 37. The parameters A_i , B_i , and C_i for EHA and ethanol were taken from Chapter 4, and the parameters for water were taken from Ref. 109.

NRTL parameters for the subsystem (EHA + ethanol) were taken from Chapter 4, where they were obtained from fits to experimental binary VLE data. The parameters for the subsystem (EHA + water) were obtained from an adjustment to the binary LLE data from this work (for details see Section 3.4). A set of parameters for the subsystem (ethanol + water) was obtained from fits to experimental binary VLE data from the literature [110–114]. The fitting procedure for the VLE was described in Section 3.4. These parameters from the three fits to binary data were used for the calculation of residue curves.

In principle, this procedure results in a complete thermodynamic model for the ternary system that allows for the prediction of the LLE in the ternary system. However, it was found that this model does not yield a sufficiently accurate description of the ternary LLE. The miscibility gap was predicted to be wider than observed experimentally. This comes at little surprise; such deviations of predictions of LLE based on activity coefficient models that were fitted to VLE data are common [115–117]. Furthermore, the simultaneous description of VLE and LLE are known to be conflicting objectives when using G^E models such as NRTL, so a sufficiently accurate representation of both types of phase equilibria might be impossible. [118] This was confirmed here, as attempts at finding a parametrization that describes all types of phase equilibria in the ternary system satisfactorily were unsuccessful. Therefore, a second set of NRTL parameters for the subsystem (ethanol + water) was optimized with respect to the ternary LLE data. These parameters were chosen as they exerted the largest influence on the shape of the miscibility gap in the ternary system. In turn, this second set of parameters does not provide a sufficiently accurate description of the VLE in the system (ethanol + water). The results for the parameters a_{ij} and b_{ij} of the NRTL model are listed in Table 38.

Table 37: Antoine parameters for EHA, ethanol, and water.

component i	A_i	B_i	C_i	Ref.
EHA	15.235	-4066.6	-117.61	[71], see Table 12
ethanol	16.497	-3571.9	-50.735	[82], see Table 12
water	16.311	-3834.0	-45.622	[109]

Table 38: NRTL model parameters a_{ij} and b_{ij} .

i, j	a_{ij}	b_{ij}	adjusted to
EHA, ethanol	-1.343	0 ^a	VLE data from this work, see Chapter 4
ethanol, EHA	2.4197	0 ^a	
EHA, water	0.2325	474.5614	binary LLE data from this work
water, EHA	5.2462	-74.3608	
ethanol, water	-0.8749	85.1817	ternary LLE data from this work
water, ethanol	3.1098	-128.6514	
ethanol, water	-0.1631	0 ^a	VLE data from the literature [110–114]
water, ethanol	1.9553	0 ^a	

^aNot needed and set to zero.

8 Simulation Study of Superheating in Evaporating Droplets of (TTIP + *p*-Xylene) in Spray Flame Synthesis

8.1 State of the Art

Several hypotheses for the causes of micro-explosions in spray flame synthesis have been proposed in the literature. Stark et al. [11] suggest that micro-explosions are caused by the rapid heating of the droplets in the flame leading to decarboxylation of carboxylic acid salt precursors. The associated release of gaseous CO₂ is believed to initiate micro-explosions. Rosebrock et al. [86] propose the following mechanism for micro-explosions: the preferential evaporation of the low-boiling solvent leads to an accumulation of higher-boiling precursor components at the droplet surface, which in turn causes a temperature increase there. This favors the thermal decomposition of the precursor into viscous intermediates. The high viscosity and the connected low mass diffusivity in the outer region of the droplet, which is referred to as a *viscous shell*, leads to the superheating of the low-boiling solvent in the droplet and, finally, to micro-explosions. The same mechanism is described by Meierhofer et al. [8]. Li et al. [33] attribute micro-explosions to a similar mechanism with shell formation. However, they claim that also solid products from the precursor decomposition reactions contribute to the shell formation, referring to the mechanism described for slurry droplet micro-explosions [119]. Skenderović et al. [120] suggest that micro-explosions are caused by the precipitation of salt precursors at the surface of the droplet, where the precursor concentration is highest. Angel et al. [64] assume that reactions between precursor and solvent components lead to the formation of explosive nitrate esters or metal carboxylates, which can release CO₂ during decarboxylation at high temperatures as also described by Stark et al. [11]. As mentioned in the Introduction, in the field of fuel combustion, the occurrence of micro-explosions of fuel droplets is usually attributed to a superheating inside the droplet. Superheating of the evaporating multicomponent fuel droplets is reported to be a consequence

of heat conduction being faster than mass diffusion, corresponding to high Lewis numbers [28, 29, 31]. While this process is challenging to observe experimentally, it can be described readily using mathematical and numerical models.

Models for droplet heating, evaporation, and combustion have been developed for several decades now, mainly focusing on applications in fuel combustion [121–126]. These models describe the temporal evolution of the properties of a single droplet in a hot atmosphere. There are models in which the droplet is represented with resolution in its radial coordinate while others assume the droplet to be well-mixed and consider only lumped droplet properties. Some of these droplet evaporation and combustion models have also been adapted for investigations of the spray flame synthesis process [19, 27, 120, 127–132]. The models are sometimes designed to be included in more complex simulations on a larger scale, such as computational fluid dynamics [127–130] or Monte-Carlo simulations of combustion [120]. Others aim at gaining a deeper insight into the processes inside the droplet [19, 27, 131].

Li et al. [27] propose a one-dimensional droplet evaporation model based on the work of Law [28] and Zhang and Law [133] to evaluate temperature and concentration profiles for optical diagnostics of single droplet combustion experiments. They study droplets consisting of SnEHA and xylene experimentally and numerically. Using the diffusion-limit approach, the liquid phase is spatially resolved and the time-dependence of the thermophysical properties is considered. However, due to the lack of property data for the system, especially for SnEHA, the properties of the pure components as well as the mixtures are only estimated.

Ren et al. [19] also base their one-dimensional model on the work of Law [28] and Zhang and Law [133]. They present a comprehensive multicomponent droplet combustion model including the precursor reaction pathways and particle formation routes. Mixtures of EHA and *m*-xylene with and without the precursor SnEHA are studied. Due to the lack of property data, the missing properties of the precursor SnEHA are assumed to be similar to those of EHA. The properties of the pure components are estimated by group contribution methods and mixture properties are calculated assuming ideal mixing behavior. The diffusion coefficients in the liquid phase are used as control parameters. Gas, liquid and solid phases are described in detail. The influence of the liquid phase Lewis number on the temperature and composition profiles and on the occurrence of micro-explosions is considered. The boiling point of the liquid mixture is examined. The micro-explosion time, which the authors define as the time until the mixture boiling point is reached in the droplet interior, is found to decrease with increasing Lewis number. In short: the results from Ren et al. [19] support the hypothesis that the micro-explosions are caused by superheating, and, because of a lack of fluid property data, they carry out parametric studies related to this phenomenon.

The model presented by Narasu et al. [130] is similar to that from their previous work [129] and based on the works of Abramzon and Sirignano [123] and Brenn et al. [134]. They study the evaporation of droplets consisting of TTIP and *p*-xylene in a hot environment with convective boundary conditions as lumped systems. Their model includes liquid phase properties based on the experimental results and correlations by Keller et al. [36]. The model was recently extended and now resolves the liquid interior spatially [131]. This extended one-dimensional model also includes a shell-formation mechanism and thereby considers induced puffing and micro-explosion events.

(TTIP + *p*-xylene) was chosen as the precursor solution in the present study because a comprehensive set of thermophysical properties is available for this system [36]. Moreover, no liquid phase reactions and no solid precipitation have been observed for this system and the decomposition of the components occurs only at high temperatures above 600 °C. [8, 135]

8.2 Evaporating Droplet Model

8.2.1 Overview

The present evaporating droplet model is inspired by the work of Faeth [121]. The droplet is spherical, all processes are radially symmetric, the radial coordinate is r . The pressure is always 1 bar. The droplet consists of two components $i = (\text{TTIP}, p\text{-xylene})$. Heat conduction and diffusion inside the droplet are described and the mass and energy balance equations are solved considering convective boundary conditions, resulting in the mole fraction profiles $x_i(r, t)$ of both components and the temperature profile $T(r, t)$. The droplet is assumed to be in convective contact with an ambient gas (g) with a constant temperature T_∞ and $y_{\infty, i} = 0$, where y_i is the mole fraction of the component i ($i = \text{TTIP}, p\text{-xylene}$) in the gas phase. The heat flow into the droplet is $\dot{Q}$, the mass flows of the evaporating components are $\dot{m}_i$ ($i = (\text{TTIP}, p\text{-xylene})$). The solubility of the gas in the liquid is neglected. The liquid phase properties — density ρ , thermal conductivity λ , isobaric heat capacity c_p , and (binary) diffusion coefficient D — depend on the temperature and the composition and, therefore, on the radial coordinate r and the time t . Additionally, the radius R of the droplet varies with time. A sketch of the model is shown in Figure 24.

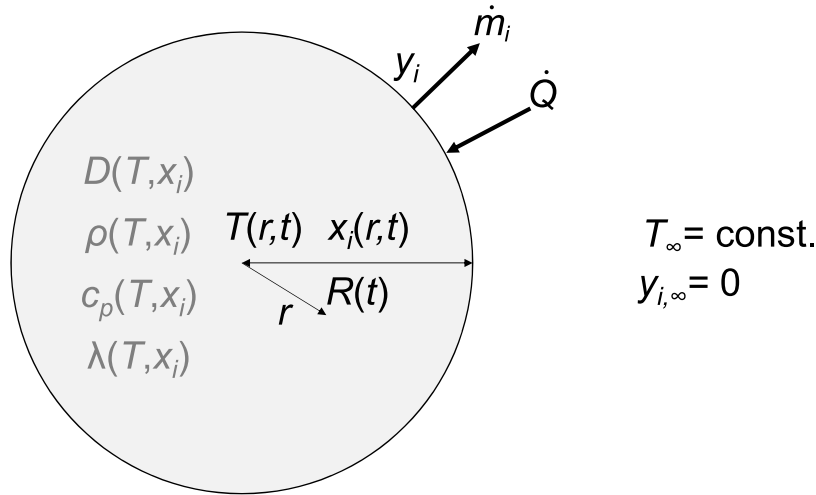


Figure 24: Sketch of the model.

8.2.2 Governing Equations

The heat transfer in the droplet is described by the one-dimensional transient heat conduction equation in spherical coordinates under consideration of variable fluid properties

(see [136]):

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_p} \left[\frac{\partial^2 T}{\partial r^2} + \left(\frac{2}{r} + \frac{1}{\lambda} \frac{\partial \lambda}{\partial r} \right) \frac{\partial T}{\partial r} \right] - T \left(\frac{1}{\rho} \frac{\partial \rho}{\partial t} + \frac{1}{c_p} \frac{\partial c_p}{\partial t} \right) \quad (28)$$

The fluid is a binary liquid mixture. The mass transfer in the droplet is analogously described by the one-dimensional transient diffusion equation for each of the two liquid phase components i , allowing for variable fluid properties [136]:

$$\frac{\partial x_i^{(m)}}{\partial t} = D \left[\frac{\partial^2 x_i^{(m)}}{\partial r^2} + \left(\frac{2}{r} + \frac{1}{\rho} \frac{\partial \rho}{\partial r} + \frac{1}{D} \frac{\partial D}{\partial r} \right) \frac{\partial x_i^{(m)}}{\partial r} \right] - x_i^{(m)} \frac{1}{\rho} \frac{\partial \rho}{\partial t} \quad (29)$$

Therein, $x_i^{(m)}$ is the mass fraction of component i and D is the binary Fickian diffusion coefficient. In the derivation of Eqs. (28) and (29) it is assumed that there is no convection inside the droplet.

8.2.3 Boundary Conditions

In the droplet center at $r = 0$, Neumann boundary conditions are applied:

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \quad (30)$$

$$\left. \frac{\partial x_i^{(m)}}{\partial r} \right|_{r=0} = 0 \quad (31)$$

At the outer radius R of the droplet, the coupling of heat and mass transfer during evaporation has to be taken into account. The time derivative of the droplet radius $R(t)$ is calculated by [136]:

$$\frac{dR}{dt} = -\frac{1}{\rho(r=R, t)R^2} \left(\sum \dot{m}_i + \int_0^R \frac{\partial \rho}{\partial t} r^2 dr \right) \quad (32)$$

Throughout this chapter, the $\sum$ sign denotes a summation over the two liquid phase components. The convective boundary conditions used here were taken from Ref. 121 and consider the presence of the gas (that is assumed to be insoluble in the liquid) in addition to the evaporating components. The evaporating mass flow $\dot{m}_i$ of component i is calculated by [121]:

$$\dot{m}_i = 2\pi R \rho_g D_{i,g} Sh_i \varepsilon_i B_M \quad (33)$$

Therein, ρ_g is the ambient gas density and $D_{i,g}$ is the diffusion coefficient of component i at infinite dilution in the ambient gas. The calculation of the Sherwood number Sh_i is described in Section 8.2.4. B_M is the Spalding mass transfer number, which is defined

as [121]:

$$B_M = \frac{\sum y_i^{(m)}}{1 - \sum y_i^{(m)}} \quad (34)$$

The partial evaporation rate ε_i is then obtained from:

$$\varepsilon_i = \frac{\dot{m}_i}{\dot{m}} = \frac{y_i^{(m)}(1 + B_M)}{B_M} \quad (35)$$

$y_i^{(m)}$ is the mass fraction of the evaporating component i in the gas phase at the droplet surface. It is calculated from the corresponding mole fraction y_i using the molar masses of the evaporating components M_i and the ambient gas molar mass M_g :

$$y_i^{(m)} = \frac{y_i M_i}{\sum y_i M_i + (1 - \sum y_i) M_g} \quad (36)$$

y_i , the mole fraction of component i in the gas phase at the droplet surface, is calculated from the vapor-liquid equilibrium at the droplet surface using the extended Raoult's law:

$$y_i = \frac{[p_i^s(T) x_i \gamma_i]_{r=R}}{p} \quad (37)$$

Therein, p_i^s is the vapor pressure of the pure component i , x_i is the liquid phase mole fraction of component i , γ_i is the activity coefficient of component i , all of which are evaluated at the outer droplet radius $r = R$, and p is the pressure.

The net heat flow into the droplet at the outer radius is given by [121]:

$$\dot{Q} = 2\pi R \lambda_g Nu (T_\infty - T(R)) - \sum \dot{m}_i \Delta h_i^{v,(m)} \quad (38)$$

The calculation of the Nusselt number Nu is described in Section 8.2.4. λ_g is the ambient gas thermal conductivity and $\Delta h_i^{v,(m)}$ is the specific enthalpy of vaporization of the component i .

8.2.4 Characteristic Heat and Mass Transfer Numbers

The characteristic heat and mass transfer numbers are calculated as suggested by Faeth [121]. The characteristic numbers are obtained from empirical correlations and subsequently corrected for convection. The equations for the uncorrected Nusselt number Nu_0 and Sherwood number $Sh_{0,i}$ of component i are:

$$Nu_0 = \left(2 + \frac{0.555 Re^{1/2} Pr^{1/3}}{\left(1 + \frac{1.232}{Re Pr^{4/3}} \right)^{1/2}} \right) \quad (39)$$

$$Sh_{0,i} = \left(2 + \frac{0.555 Re^{1/2} Sc_i^{1/3}}{\left(1 + \frac{1.232}{Re Sc_i^{4/3}} \right)^{1/2}} \right) \quad (40)$$

The Reynolds number Re is given by

$$Re = \frac{u \rho_g 2R}{\eta_g} \quad (41)$$

with the droplet velocity u and the viscosity of the ambient gas η_g . The Prandtl number Pr and Schmidt number Sc_i of component i are calculated by:

$$Pr = \frac{\eta_g c_{p,g}}{\lambda_g} \quad (42)$$

$$Sc_i = \frac{\eta_g}{\rho_g D_{i,g}} \quad (43)$$

$c_{p,g}$ is the isobaric heat capacity of the ambient gas and $D_{i,g}$ is, again, the diffusion coefficient of component i at infinite dilution in the ambient gas.

These Nusselt and Sherwood numbers are subsequently corrected for convection using the Spalding mass transfer number B_M (see Eq. (34)) and the Spalding heat transfer number B_T , which is given by:

$$B_T = \frac{\bar{c}_{p,v}(T_\infty - T(R))}{2\pi R \lambda_g Nu (T_\infty - T(R))/\dot{m} + \sum \Delta h_i^{v,(m)}} \quad (44)$$

Therein, $\bar{c}_{p,v} = \sum \varepsilon_i c_{p,v,i}$ is the mass flux-weighted average heat capacity of the evaporating species in the vapor phase. The equations for the Nusselt and Sherwood numbers with convection correction are:

$$Nu = Nu_0 \frac{\ln(1 + B_T)}{B_T} \quad (45)$$

$$Sh_i = Sh_{0,i} \frac{\ln(1 + B_M)}{B_M} \quad (46)$$

8.2.5 Property Models

8.2.5.1 Liquid Phase

In this study, the liquid phase is a binary mixture of TTIP and *p*-xylene. The density, thermal conductivity, isobaric heat capacity, and self-diffusion coefficients in liquid mixtures of TTIP and *p*-xylene were calculated from the correlations provided by Keller et al. [36]. The enthalpy of vaporization was calculated using the Clausius-Clapeyron

equation and from the vapor pressure curves given in Ref. 36. The activity coefficients for vapor-liquid equilibrium calculations were evaluated from the non-random two liquid (NRTL) model with parameters taken from Keller et al. [36]. The Fickian diffusion coefficient was calculated as described in Section 3.2.

8.2.5.2 Gas Phase

The gas phase in the model consists of pure oxygen. The gas phase properties of oxygen were calculated as follows. The density ρ_g was obtained from the ideal gas law. The viscosity η_g was calculated using Lucas's method [54]. The thermal conductivity λ_g and the isobaric heat capacity $c_{p,g}$ were calculated using correlations and parameters from Ref. 137. The diffusion coefficients $D_{i,g}$ of TTIP and *p*-xylene in oxygen were estimated by Fuller's method [54]. The isobaric heat capacities of TTIP and *p*-xylene in the vapor phase $c_{p,v,i}$, which are only needed in Eq. (44), were calculated using NASA polynomials [138] with parameters taken from Refs. [139] and [140].

8.2.6 Implementation

For the solution of the model equations, an explicit finite-difference scheme with forward differences in time with adaptive step size and second-order central differences in space was applied. To ensure the numerical stability of the finite-difference scheme, the following criterion was applied to calculate the time increment Δt for every iteration:

$$\Delta t = 0.1 \min \left(\frac{(\Delta r)^2}{\max(a)}, \frac{(\Delta r)^2}{\max(D)} \right) \quad (47)$$

Therein, Δr is the spatial grid size calculated from the current droplet radius R and the number of spatial grid points. The liquid thermal diffusivity $a = \frac{\lambda}{\rho c_p}$ and the liquid diffusion coefficient D were evaluated at each spatial grid point and the maximum value was used for the calculation of the time increment. The model was set up with 100 spatial nodes and the calculation was terminated when the droplet radius reached 4 μm . The evaporating droplet model and the property models were implemented in `python` using the modules `numpy`, `pandas`, and `scipy`.

8.3 Lewis Number

Figure 25 shows the Lewis number Le of (TTIP + p -xylene) mixtures as a function of the p -xylene mole fraction at different temperatures. The Lewis number Le was calculated using correlations from Ref. 36 and the Fickian diffusion coefficient (cf. Section 3.2). Le is significantly larger than 40 in all cases. Therefore, the heat conduction is always much faster than the mass diffusion, which makes the occurrence of superheating phenomena during the evaporation of a (TTIP + p -xylene) droplet likely.

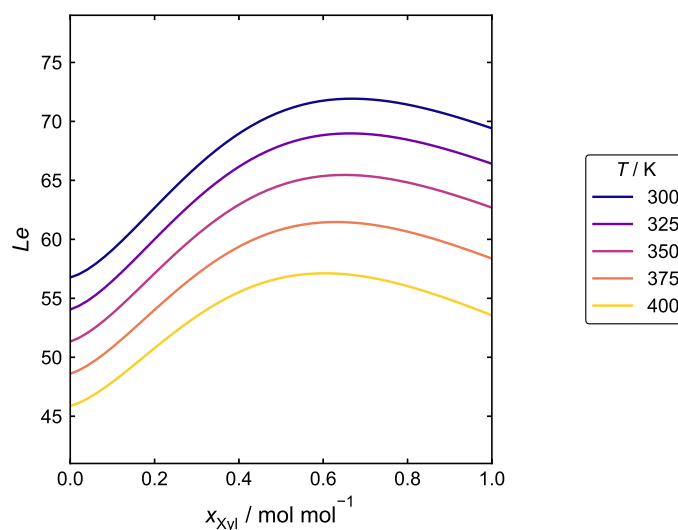


Figure 25: Lewis number of (TTIP + p -xylene) mixtures as a function of the p -xylene mole fraction at different temperatures.

8.4 Simulation Results and Discussion

8.4.1 Scenarios

Two types of evaporation scenarios with different initial and boundary conditions of the model were considered. The input parameters differing between the two scenarios are the initial droplet diameter d_0 , the initial droplet composition $x_{\text{TTIP},0}$ (which was assumed to be uniform), the droplet velocity u , and the ambient temperature T_∞ . The latter two were constant during each simulation.

First, these initial and boundary conditions were chosen to emulate the conditions of single droplet combustion experiments. Experimental results for single droplet combustion of droplets containing TTIP and a xylene isomer mixture were reported by Li et al. [33]. In their experimental setup, the ambient temperature is unknown, but is most likely room temperature and the droplets are heated by the spherical flame surrounding them. Combustion processes are not included in the model presented in this work. Therefore, different ambient temperatures were considered for emulating this case, ranging from 1000 to 2750 K.

Second, the initial and boundary conditions were set to represent the conditions during flame spray combustion. In this case, the initial droplet sizes are smaller and the droplet velocity is much higher than for the single droplet combustion experiments. Despite the fact that in reality, the droplet velocity and the local temperature of the ambient gas phase vary along the droplet's trajectory [141], this was neglected and constant boundary conditions were used. The initial droplet size, the droplet velocity, and the ambient temperature were set to typical average values for the spray flame combustion process [15, 26, 128, 141]. The initial composition was varied within the range reported in the literature for (TTIP + xylene) precursor solutions [8, 142–144].

In all simulation scenarios studied in this work, the (uniform) initial droplet temperature was 300 K. An overview of the initial and boundary conditions of the simulations is given in Table 39.

Table 39: Initial and boundary conditions applied in the simulations.

Case		d_0 / μm	$x_{\text{TTIP},0}$ mol mol ⁻¹	u / m s ⁻¹	T_∞ / K
Single droplet combustion	Ia	86	0	0.5	1000 – 2750
	Ib	91	0.07 ^a		
Spray flame combustion	II	20	0.01 – 0.3	50	2000

^aCorresponding to an initial TTIP concentration of 0.5 mol L⁻¹.

8.4.2 Results for the Droplet Diameter

The results for the droplet diameter as a function of time are discussed first. The time span between the start of the simulation and its termination, which is reached when the droplet radius has decreased to $4\text{ }\mu\text{m}$, is referred to as droplet lifetime in this work.

Figure 26 shows the experimental results from single droplet combustion experiments by Li et al. [33] and simulation results of the present work that were obtained for initial and boundary conditions that were similar, although not the same, as in the corresponding experiment (cf. Table 39, cases Ia and Ib). The normalized squared droplet diameter $(d/d_0)^2$ is shown as a function of the normalized time t/d_0^2 , which has been shown to allow for a straightforward comparison of droplets with different initial sizes [122, 130]. As expected, the evaporation process is slower at lower ambient temperatures. The general course of the curves in Figure 26 is similar. For most of the droplet lifetime, the decrease of the droplet size follows the well-known d^2 -law [122]. This is in agreement with the experimental results. However, the simulation underestimates the evaporation rate, even for the highest studied temperature. This could be caused by an underestimation of the heat and mass transfer rates between the droplet and the gas phase (i.e., by the boundary conditions), but there are also other possible reasons, such as the simplified mass transfer model inside the droplet. Nevertheless, the model is confirmed qualitatively by the comparison with the experimental data. The quantitative description of this single experiment was not pursued, which would have required a reparameterization of the model.

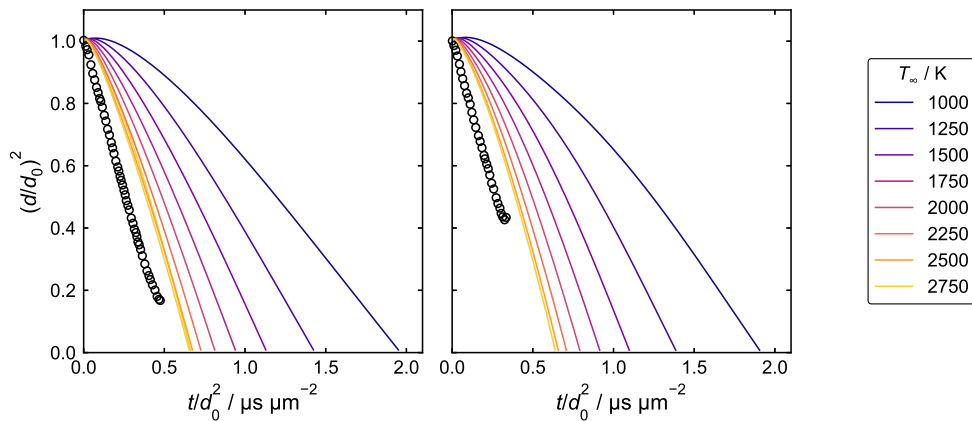


Figure 26: Normalized squared droplet diameters as a function of the normalized time for pure *p*-xylene (left, case Ia cf. Table 39) and 0.5 M TTIP ($\approx 0.07\text{ mol mol}^{-1}$) in *p*-xylene (right, case Ib cf. Table 39). Symbols: experimental results [33]. Lines: simulation results.

Figure 27 presents the simulation results for the second type of initial and boundary conditions (case II) essentially in the same way as in Figure 26. However, no experimental data are available for comparison. Results are shown for different initial TTIP

mole fractions $x_{\text{TTIP},0}$; the ambient gas temperature is always 2000 K. The shape of the curves is similar as in Figure 26. The droplet lifetime increases slightly with increasing initial TTIP mole fraction, but the overall influence of the initial composition is small. Owing to the scaling of the droplet lifetime with the droplet radius, the normalized droplet lifetime is almost the same as the corresponding previous result at the same temperature from Figure 26, even though the droplet velocity is much higher in case II.

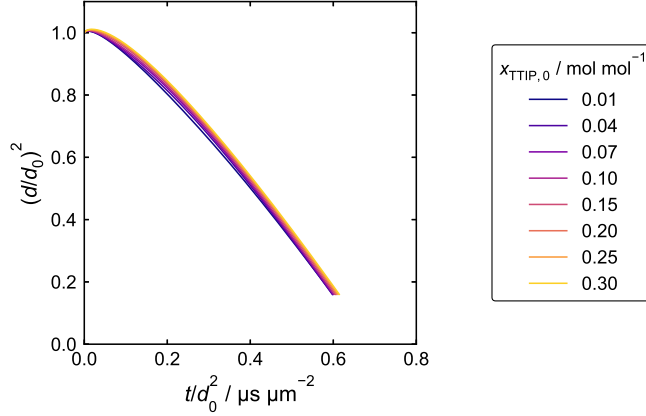


Figure 27: Simulation results for case II from Table 39: normalized squared droplet diameters as a function of the normalized time.

8.4.3 Results for Temperature, Composition, and Superheating

The spatially resolved temperature and composition profiles in the droplet obtained from the simulation allow to investigate if the liquid is superheated at any position inside the droplet. For this purpose, the vapor pressure of the liquid at the given temperature and composition was compared to the total pressure p . As the pressure difference between the droplet and its surroundings due to the droplet curvature is small for droplet sizes in the micrometer range as they are studied here, the total pressure was always set to 1 bar. Due to the lack of sufficient data for the surface tension of mixtures of TTIP and *p*-xylene, the detailed quantification of this effect is not possible, which is why the simulations were terminated at $R = 4 \mu\text{m}$ as described above, where the influence of the droplet curvature on the internal pressure is still negligible. For characterizing the superheating, the so-called superheating index S is defined as follows:

$$S = \sum p_i^s(T) x_i \gamma_i / p \quad (48)$$

For $S > 1$, the liquid is superheated and boiling may set in. The superheating index is calculated using the local temperature and composition at each spatial grid point for each

time step. Therefore, the profiles of the superheating index shown in this subsection are an immediate implication of the corresponding temperature and composition profiles.

Figures 28 and 29 show the results for temperature, composition, and superheating index for cases Ia and Ib (cf. Table 39) for an ambient temperature of 2000 K. Figure 28 shows results for the evaporation of a pure *p*-xylene droplet. As expected, the droplet temperature increases most rapidly at the surface and approaches the boiling temperature of *p*-xylene at 1 bar (412 K [27, 36]). The temperature in the center of the droplet increases more slowly. For pure components, the vapor pressure depends only on the temperature, so that the superheating index S is directly related to the temperature. Unsurprisingly, the maximum of the superheating index S , which is located at the droplet surface, never exceeds 1 during the entire studied evaporation process.

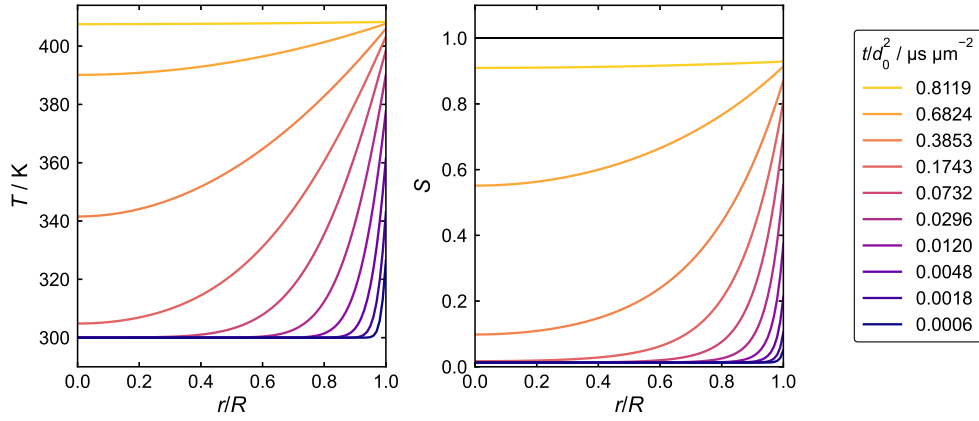


Figure 28: Simulation results for case Ia from Table 39 (pure *p*-xylene): temperature (left) and superheating index (right) in the droplet interior as a function of the dimensionless droplet radius at different normalized times. The ambient temperature is $T_\infty = 2000$ K.

Figure 29 shows the results for an evaporating (TTIP + *p*-xylene) droplet (case Ib). The temperature profiles are similar to those observed for the pure *p*-xylene droplet (cf. Figure 28) at first, but towards the end of the droplet lifetime, a temperature gradient close to the droplet surface remains, whereas the temperature of the pure *p*-xylene droplet becomes uniform eventually. The mole fraction of the low-boiling component *p*-xylene decreases strongly at the surface, while the composition in the center of the droplet remains basically unchanged throughout the entire droplet lifetime, due to the slow diffusive mass transfer in the liquid phase. The difference between the shapes of temperature and composition profiles is a consequence of the high Lewis numbers in the liquid phase (cf. Figure 25). The comparatively high thermal diffusivity leads to significant heat conduction to the droplet center. In contrast, the mass diffusion is slow, which leads to the depletion of the low-boiling *p*-xylene at the surface over time. As a result of the interplay of the temperature and the composition profiles, maxima appear

in the profiles of the superheating index. These maxima are located close to the droplet surface at all times during the evaporation process and can exceed $S = 1$ from a certain time onward.

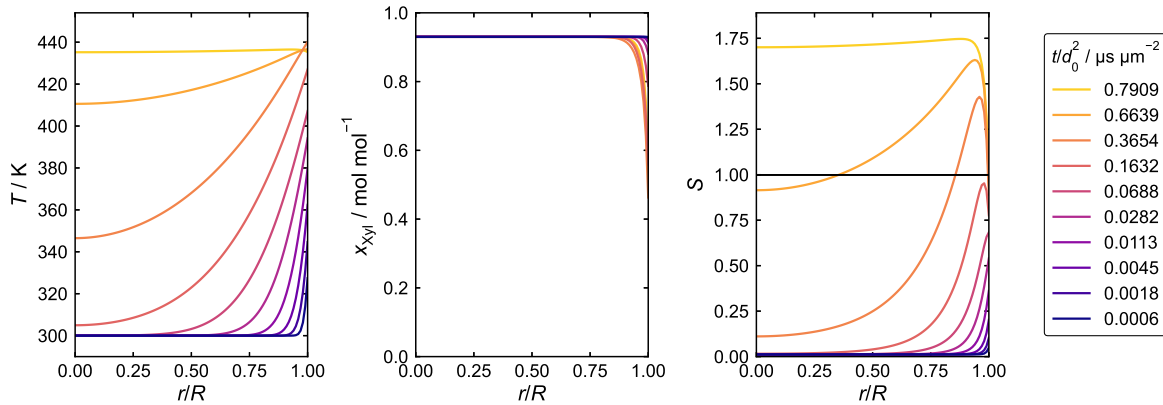


Figure 29: Simulation results for case Ib from Table 39: temperature (left), *p*-xylene mole fraction (center), and superheating index (right) in the droplet interior as a function of the dimensionless droplet radius at different normalized times. The ambient temperature is $T_\infty = 2000$ K.

Figure 30 shows the temperature, composition, and superheating index profiles for the evaporation of a (TTIP + *p*-xylene) droplet under initial and boundary conditions representing the spray flame case (case II, cf. Table 39). The initial TTIP mole fraction is $x_{\text{TTIP},0} = 0.07 \text{ mol mol}^{-1}$. The profiles are almost similar to those in Figure 29. Again, the temperature rises more quickly at the surface than in the center of the droplet, the composition only changes close to the surface, and, therefore, the formation of a pronounced maximum of the superheating index S is observed, which also reaches values above 1 in the droplet lifetime. This indicates that superheating can occur at the conditions in spray flame synthesis.

8.4.4 Results for the Superheating Maxima

In this subsection, the results for the superheating index are discussed in more detail. Vaporization can in principle set in anytime at any position where $S > 1$. In practice, however, a certain threshold in S must be exceeded for bubble nucleation to set in. The spinodal gives an upper limit of S , above which nucleation will occur instantaneously, but it must be expected that nucleation sets in well before that limit is reached. The exact point of the onset of nucleation is difficult to predict, as it depends on many parameters, such as the rate at which S changes and the purity of the mixture. Therefore, different values of the superheating index are considered ($S^* \geq 1, 1.4, 1.6, 1.8$). For all simulations of evaporating mixture droplets (cf. Table 39, cases Ib and II), the time

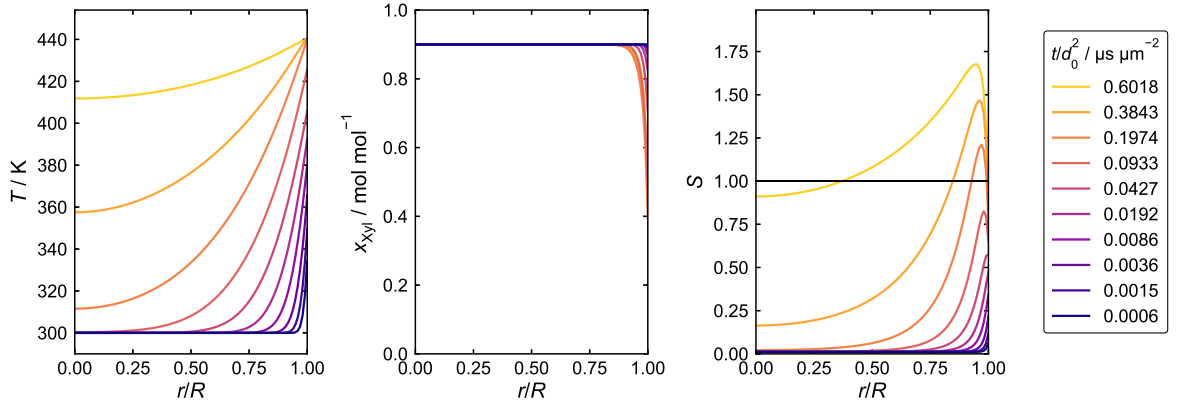


Figure 30: Simulation results for case II from Table 39: temperature (left), *p*-xylene mole fraction (center), and superheating index (right) in the droplet interior as a function of the dimensionless droplet radius at different normalized times. The initial TTIP mole fraction is $x_{\text{TTIP},0} = 0.07 \text{ mol mol}^{-1}$.

and dimensionless droplet radius for which these thresholds of the superheating index S^* are reached for the first time were determined.

The position at which vapor nucleation occurs is important for the micro-explosion event. Two basic modes of the micro-explosions have been described in the literature [25–27, 87]: in the first mode, which is sometimes called puffing, a fog-like swarm of small droplets is ejected from the droplet at a certain position, but otherwise the parent droplet remains largely intact. The change of momentum upon the ejection leads to an abrupt change in the flight direction of the parent droplet. In the second mode, the parent droplet is torn apart and dispersed into a large number of smaller droplets flying in different directions. These modes can be associated with the position in the droplet, where the sudden evaporation sets in: the first mode (puffing) is expected, when the evaporation occurs close to the droplet's surface, whereas the second mode is expected when the evaporation sets in deeper in the droplet.

Figure 31 shows the results for the "single droplet combustion" (case Ib, cf. Table 39) for different ambient temperatures. As expected, the superheating index threshold is reached more quickly when the ambient temperature increases and it takes longer to reach higher thresholds (cf. left panel in Figure 31). $S^* \geq 1.8$ is reached only for ambient temperatures below 2000 K, likely due to the longer droplet lifetimes at lower temperatures. The position at which a given superheating index is reached first (cf. right panel of Figure 31) depends both on the ambient temperature T_∞ and the value of S^* . For low T_∞ , the position moves inside the droplet, and the same holds for larger values of S^* . However, in most studied cases the onset of vaporization occurs rather close to the droplet surface ($r/R > 0.8$), which indicates a preference for puffing. This is in agreement with results by Li et al. [87], who observe surface micro-explosions in single

droplet combustion experiments with the precursor solution tin (II) 2-ethylhexanoate in xylene, where the outer layer of a droplet is ejected while the inner part of the droplet continues to evaporate and combust. Also, high-speed camera images of exploding droplets of (TTIP + xylene) from Ref. 33 indicate puffing, see supporting information of Ref. 33.

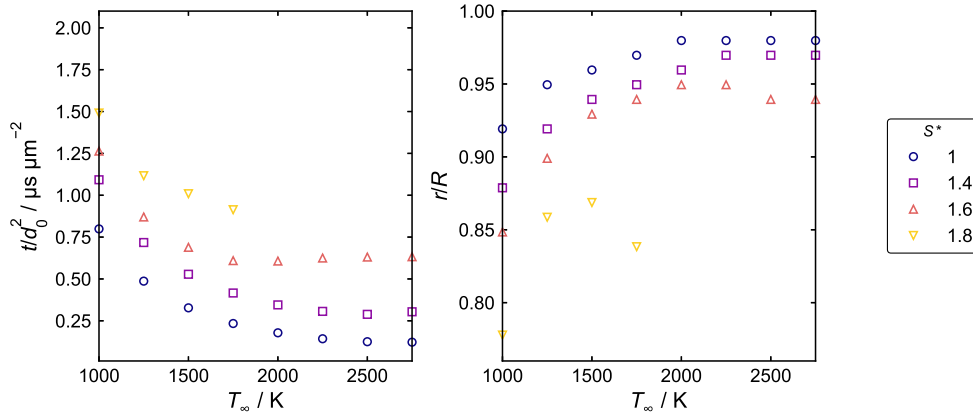


Figure 31: Simulation results for case Ib from Table 39: normalized time (left) and dimensionless droplet radius (right) at which the superheating index first reaches the thresholds indicated in the legend as a function of the ambient temperature. The open symbols show results of individual simulation runs.

Figure 32 shows the corresponding results for the "spray flame combustion" (case II, cf. Table 39) for different initial TTIP mole fractions. The time needed until the threshold is reached (cf. left panel in Figure 32) decreases with increasing initial TTIP mole fraction, in agreement with observations from single droplet combustion experiments, where higher precursor concentrations lead to an earlier onset of micro-explosions [33]. At higher initial TTIP concentrations, the influence of the composition on the time of the onset of vaporization is weaker, even a shallow minimum is observed.

Only the lowest threshold is reached within the droplet lifetime for the lowest initial TTIP mole fraction $x_{\text{TTIP},0} = 0.01 \text{ mol mol}^{-1}$. Additionally, the values $S^* = 1.4$, $S^* = 1.6$, and $S^* = 1.8$ are also not reached for $x_{\text{TTIP},0} < 0.07 \text{ mol mol}^{-1}$, $x_{\text{TTIP},0} < 0.1 \text{ mol mol}^{-1}$, and $x_{\text{TTIP},0} < 0.15 \text{ mol mol}^{-1}$, respectively. These findings suggest that the occurrence of micro-explosions requires a certain minimum precursor concentration, which is in accord with practical experience. The position where the threshold is reached (cf. right panel in Figure 32) generally depends only weakly on the initial TTIP mole fraction for a given S^* . The radial positions where the thresholds are reached tend to move slightly towards the droplet interior for higher thresholds. However, in all simulations the positions where S^* is reached first is at $r/R > 0.9$, i.e., near to the droplet surface, indicating a tendency for puffing micro-explosions.

It is not trivial to understand the details of the influence of $x_{\text{TTIP},0}$ on the results pre-

sented in Figure 32, but it is clear, that the influence is important, as higher thresholds require higher initial TTIP mole fractions. Superheating also occurs earlier for higher initial TTIP mole fractions. If superheating occurs only close to the end of the droplet lifetime, the influence of the possibly resulting micro-explosion event on the particle synthesis process is likely less important than if the micro-explosions occurs while the droplet is still large. [24] Therefore, a certain minimum initial TTIP content is probably necessary to (a) achieve the necessary level of superheating for a micro-explosion to occur and (b) lead to micro-explosions early enough to have a significant impact on the mass transfer of the precursor from the liquid droplets to the gas phase.

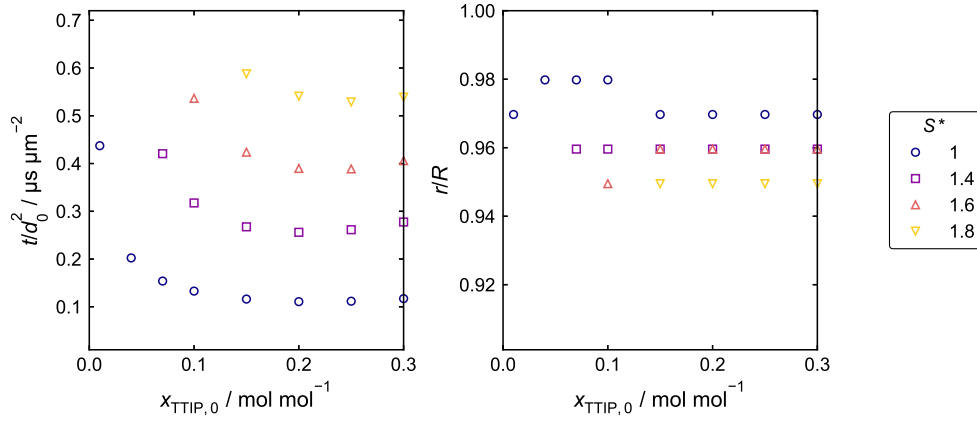


Figure 32: Simulation results for case II from Table 39: normalized time (left) and dimensionless droplet radius (right) at which the superheating index first reaches the thresholds indicated in the legend as a function of the initial TTIP mole fraction. The open symbols show results of individual simulation runs.

9 Conclusions

In this work, the thermophysical properties of binary mixtures of (EHA + ethanol), (EHA + *p*-xylene), and (SnEHA + *p*-xylene) were investigated experimentally, which are relevant for research and development of spray flame synthesis processes but were not available in the literature. Correlations were developed for the density, viscosity, thermal conductivity, isobaric heat capacity, and the self-diffusion coefficients of both components in each mixture. In addition, VLE in mixtures of (EHA + ethanol) and (EHA + *p*-xylene) and LLE in mixtures of (EHA + ethanol + water) were investigated and the parameters for NRTL models were adjusted to the experimental results. The results of this work can be used in models and simulations of spray flame synthesis.

Simulations can provide both a means for design and optimization of spray flame synthesis processes and, more specifically, a deeper understanding of the reasons of micro-explosions during droplet evaporation in the spray flame, which are linked to the output of functional and valuable product nanoparticles. A simple one-dimensional model of an evaporating single droplet was developed that is suited for conceptual studies of spray flame processes, namely on investigating the reasons of the micro-explosions and the influence of process parameters such as the precursor solution properties on their occurrence. With this model, a simulation study of evaporating droplets consisting of mixtures of (TTIP + *p*-xylene) was carried out based on detailed information on the fluid properties. The results show that superheating sets in inside the droplet. In this study, superheated states were observed mostly in the vicinity of the droplet surface, suggesting that so-called surface micro-explosions or puffing events are dominant in the system (TTIP + *p*-xylene), which is in agreement with experimental observations from the literature. The model results provide an explanation for the droplet micro-explosions: the fact that the heat conduction is much faster than the diffusion in typical precursor solutions leads to the occurrence of superheating inside the droplet, which can eventually lead to the nucleation of a vapor bubble inside the droplet and thereby induce a micro-explosion. More precisely, the slow mass transfer causes a depletion of the low-boiling component and an accumulation of the high-boiling component near the droplet surface. Owing to the relatively fast heat transfer, the continued heat supply from the hot atmosphere not only leads to a temperature increase in the outer regions, but also in the droplet interior. Therefore, droplets composed of mixtures with wide-

boiling VLE are susceptible to superheating. In addition, a mismatch of diffusive heat and mass transport rates is required, which is indicated by high Lewis numbers. High Lewis numbers were found not only for mixtures of (TTIP + *p*-xylene): from the results of the property measurements presented in this work, the Lewis numbers were calculated and high values were observed for all investigated mixtures. Since, in addition, wide-boiling and zeotropic VLE were observed, the occurrence of internal superheating and micro-explosions during droplet evaporation is likely.

The data and methods established in this work provide a basis for further studies in the field of spray flame synthesis. Since the fluid property data provided cover the entire composition range and different temperatures, they can not only be used in the framework of the droplet evaporation model developed in this work (or a refined version thereof), but they will also prove to be useful for studying other important aspects of the processing of the precursor solution, such as spray atomization. This work provides a structured approach that can be applied to studies of other precursor solutions in the future. Ultimately, the findings of this work pave the way for a deeper understanding of the complex processes involved in spray flame synthesis and for model-based process analysis, optimization, and design.

Literature

- [1] W. Y. Teoh, R. Amal, L. Mädler: Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication, *Nanoscale* 2 (2010) 1324. DOI: 10.1039/c0nr00017e.
- [2] S. Pokhrel, L. Mädler: Flame-made Particles for Sensors, Catalysis, and Energy Storage Applications, *Energy and Fuels* 34 (2020) 13209–13224. DOI: 10.1021/acs.energyfuels.0c02220.
- [3] T. Samerjai, N. Tamaekong, K. Wetchakun, V. Kruefu, C. Liewhiran, C. Siriwong, A. Wisitsoraat, S. Phanichphat: Flame-spray-made metal-loaded semiconducting metal oxides thick films for flammable gas sensing, *Sensors and Actuators, B: Chemical* 171–172 (2012) 43–61. DOI: 10.1016/j.snb.2012.05.052.
- [4] C. Liewhiran, N. Tamaekong, A. Wisitsoraat, A. Tuantranont, S. Phanichphant: Ultra-sensitive H₂ sensors based on flame-spray-made Pd-loaded SnO₂ sensing films, *Sensors and Actuators B: Chemical* 176 (2013) 893–905. DOI: 10.1016/j.snb.2012.10.087.
- [5] M. Punginsang, A. Wisitsora-At, A. Tuantranont, S. Phanichphant, C. Liewhiran: Effects of cobalt doping on nitric oxide, acetone and ethanol sensing performances of FSP-made SnO₂ nanoparticles, *Sensors and Actuators, B: Chemical* 210 (2015) 589–601. DOI: 10.1016/j.snb.2015.01.028.
- [6] S. H. Choi, Y. C. Kang: Ultrafast synthesis of yolk-shell and cubic NiO nanopowders and application in lithium ion batteries, *ACS Applied Materials and Interfaces* 6 (2014) 2312–2316. DOI: 10.1021/am404232x.
- [7] O. Waser, M. Hess, A. Güntner, P. Novák, S. E. Pratsinis: Size controlled CuO nanoparticles for Li-ion batteries, *Journal of Power Sources* 241 (2013) 415–422. DOI: 10.1016/j.jpowsour.2013.04.147.
- [8] F. Meierhofer, H. Li, M. Gockeln, R. Kun, T. Grieb, A. Rosenauer, U. Fritsching, J. Kiefer, J. Birkenstock, L. Mädler, S. Pokhrel: Screening precursor-solvent combinations for Li₄Ti₅O₁₂ energy storage material using flame spray pyrolysis,

- ACS Applied Materials and Interfaces 9 (2017) 37760–37777. DOI: 10.1021/acsami.7b11435.
- [9] M. S. Lord, M. S. Jung, W. Y. Teoh, C. Gunawan, J. A. Vassie, R. Amal, J. M. Whitelock: Cellular uptake and reactive oxygen species modulation of cerium oxide nanoparticles in human monocyte cell line U937, *Biomaterials* 33 (2012) 7915–7924. DOI: 10.1016/j.biomaterials.2012.07.024.
- [10] M. F. Stodt, C. Liu, S. Li, L. Mädler, U. Fritsching, J. Kiefer: Phase-selective laser-induced breakdown spectroscopy in flame spray pyrolysis for iron oxide nanoparticle synthesis, *Proceedings of the Combustion Institute* (2020). DOI: 10.1016/j.proci.2020.06.092.
- [11] W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, A. Baiker: Flame synthesis of nanocrystalline ceria-zirconia: Effect of carrier liquid, *Chemical Communications* 3 (2003) 588–589. DOI: 10.1039/b211831a.
- [12] G. L. Chiarello, M. V. Dozzi, M. Scavini, J. D. Grunwaldt, E. Selli: One step flame-made fluorinated Pt/TiO₂ photocatalysts for hydrogen production, *Applied Catalysis B: Environmental* 160–161 (2014) 144–151. DOI: 10.1016/j.apcatb.2014.05.006.
- [13] C. Liu, S. Pokhrel, C. Tessarek, H. Li, M. Schowalter, A. Rosenauer, M. Eickhoff, S. Li, L. Mädler: Rare-Earth-Doped Y₄Al₂O₉ Nanoparticles for Stable Light-Converting Phosphors, *ACS Applied Nano Materials* 3 (2020) 699–710. DOI: 10.1021/acsanm.9b02231.
- [14] R. Mueller, L. Mädler, S. E. Pratsinis: Nanoparticle synthesis at high production rates by flame spray pyrolysis, *Chemical Engineering Science* 58 (2003) 1969–1976. DOI: 10.1016/S0009-2509(03)00022-8.
- [15] A. J. Gröhn, S. E. Pratsinis, A. Sánchez-Ferrer, R. Mezzenga, K. Wegner: Scale-up of nanoparticle synthesis by flame spray pyrolysis: The high-temperature particle residence time, *Industrial and Engineering Chemistry Research* 53 (2014) 10734–10742. DOI: 10.1021/ie501709s.
- [16] F. Meierhofer, L. Mädler, U. Fritsching: Nanoparticle evolution in flame spray pyrolysis—Process design via experimental and computational analysis, *AIChE Journal* 66 (2020). DOI: 10.1002/aic.16885.
- [17] F. Meierhofer, U. Fritsching: Synthesis of metal oxide nanoparticles in flame sprays: Review on process technology, modeling, and diagnostics, *Energy and Fuels* 35 (2021) 5495–5537. DOI: 10.1021/acs.energyfuels.0c04054.

- [18] R. Strobel, S. E. Pratsinis: Effect of solvent composition on oxide morphology during flame spray pyrolysis of metal nitrates, *Physical Chemistry Chemical Physics* 13 (2011) 9246–9252. DOI: 10.1039/c0cp01416h.
- [19] Y. Ren, J. Cai, H. Pitsch: Theoretical single-droplet model for particle formation in flame spray pyrolysis, *Energy and Fuels* 35 (2021) 1750–1759. DOI: 10.1021/acs.energyfuels.0c03669.
- [20] A. T. Güntner, V. Koren, K. Chikkadi, M. Righettoni, S. E. Pratsinis: E-Nose Sensing of Low-ppb Formaldehyde in Gas Mixtures at High Relative Humidity for Breath Screening of Lung Cancer?, *ACS Sensors* 1 (2016) 528–535. DOI: 10.1021/acssensors.6b00008.
- [21] C. Liewhiran, N. Tamaekong, A. Wisitsoraat, S. Phanichphant: Highly selective environmental sensors based on flame-spray-made SnO₂ nanoparticles, *Sensors and Actuators, B: Chemical* 163 (2012) 51–60. DOI: 10.1016/j.snb.2011.12.097.
- [22] M. F. Stodt, M. Gonchikzhapov, T. Kasper, U. Fritsching, J. Kiefer: Chemistry of iron nitrate-based precursor solutions for spray-flame synthesis, *Physical Chemistry Chemical Physics* 21 (2019) 24793–24801. DOI: 10.1039/c9cp05007h.
- [23] S. Angel, F. Schneider, S. Apazeller, W. Kaziur-Cegla, T. C. Schmidt, C. Schulz, H. Wiggers: Spray-flame synthesis of LaMO₃ (M = Mn, Fe, Co) perovskite nanomaterials: Effect of spray droplet size and esterification on particle size distribution, *Proceedings of the Combustion Institute* 38 (2021) 1279–1287. DOI: 10.1016/j.proci.2020.07.116.
- [24] A. Witte, L. Mädler: Single droplet combustion of iron nitrate-based precursor solutions: Investigation of time- and size scales of isolated burning FSP-droplets, *Applications in Energy and Combustion Science* 14 (2023) 100147. DOI: 10.1016/j.jaecs.2023.100147.
- [25] C. D. Rosebrock, T. Wriedt, L. Mädler, K. Wegner: The role of microexplosions in flame spray synthesis for homogeneous nanopowders from low-cost metal precursors, *AIChE Journal* 62 (2016) 381–391. DOI: 10.1002/aic.15056.
- [26] N. Jüngst, G. J. Smallwood, S. A. Kaiser: Visualization and image analysis of droplet puffing and micro-explosion in spray-flame synthesis of iron oxide nanoparticles, *Experiments in Fluids* 63 (2022) 60. DOI: 10.1007/s00348-022-03411-y.

- [27] Z. Li, D. Zhao, Y. Zhuang, F. Yang, X. Liu, Y. Chen: Volumetric properties of monoethanolamine and alcohol binary mixtures at different temperatures and 0.1 MPa, *The Journal of Chemical Thermodynamics* 133 (2019) 37–45. DOI: 10.1016/J.JCT.2019.01.025.
- [28] C. K. Law: Internal boiling and superheating in vaporizing multicomponent droplets, *AIChE Journal* 24 (1978) 626–632. DOI: 10.1002/aic.690240410.
- [29] J. C. Lasheras, A. C. Fernandez-Pello, F. L. Dryer: Experimental Observations on the Disruptive Combustion of Free Droplets of Multicomponent Fuels, *Combustion Science and Technology* 22 (1980) 195–209. DOI: 10.1080/00102208008952383.
- [30] S. K. Aggarwal: Modeling of a dilute vaporizing multicomponent fuel spray, *International Journal of Heat and Mass Transfer* 30 (1987) 1949–1961. DOI: 10.1016/0017-9310(87)90253-5.
- [31] M. Botero, Y. Huang, D. Zhu, A. Molina, C. Law: Synergistic combustion of droplets of ethanol, diesel and biodiesel mixtures, *Fuel* 94 (2012) 342–347. DOI: 10.1016/j.fuel.2011.10.049.
- [32] A. Hoxie, R. Schoo, J. Braden: Microexplosive combustion behavior of blended soybean oil and butanol droplets, *Fuel* 120 (2014) 22–29. DOI: 10.1016/j.fuel.2013.11.036.
- [33] H. Li, C. D. Rosebrock, N. Riefler, T. Wriedt, L. Mädler: Experimental investigation on microexplosion of single isolated burning droplets containing titanium tetraisopropoxide for nanoparticle production, *Proceedings of the Combustion Institute* 36 (2017) 1011–1018. DOI: 10.1016/j.proci.2016.09.017.
- [34] J. W. Leenslag, A. J. Pennings: Synthesis of high-molecular-weight poly(L-lactide) initiated with tin 2-ethylhexanoate, *Die Makromolekulare Chemie* 188 (1987) 1809–1814. DOI: 10.1002/macp.1987.021880804.
- [35] A. Kowalski, A. Duda, S. Penczek: Kinetics and Mechanism of Cyclic Esters Polymerization Initiated with Tin(II) Octoate. 3. Polymerization of L-Dilactide, *Macromolecules* 33 (2000) 7359–7370. DOI: 10.1021/ma000125o.
- [36] A. Keller, I. Wlokas, M. Kohns, H. Hasse: Thermophysical properties of mixtures of titanium(IV) isopropoxide (TTIP) and *p*-xylene, *Journal of Chemical and Engineering Data* 65 (2020) 869–876. DOI: 10.1021/acs.jced.9b01059.
- [37] A. Keller, I. Wlokas, M. Kohns, H. Hasse: Thermophysical Properties of Solutions of Iron(III) Nitrate Nonahydrate in Mixtures of 1-Propanol and Water, *Journal*

- of Chemical and Engineering Data 65 (2020) 5413–5420. DOI: 10.1021/acs.jced.0c00531.
- [38] A. Keller, I. Wlokas, M. Kohns, H. Hasse: Thermophysical properties of solutions of iron(III) nitrate-nonahydrate in mixtures of ethanol and water, Journal of Chemical and Engineering Data 65 (2020) 3519–3527. DOI: 10.1021/acs.jced.0c00105.
- [39] A. Keller, I. Wlokas, M. Kohns, H. Hasse: Thermophysical properties of mixtures of titanium(IV) isopropoxide (TTIP) and 2-propanol (iPOH), Journal of Chemical and Engineering Data 66 (2021) 1296–1304. DOI: 10.1021/acs.jced.0c00941.
- [40] D. Bellaire, H. Kiepfer, K. Münnemann, H. Hasse: PFG-NMR and MD simulation study of self-diffusion coefficients of binary and ternary mixtures containing cyclohexane, ethanol, acetone, and toluene, Journal of Chemical and Engineering Data 65 (2020) 793–803. DOI: 10.1021/acs.jced.9b01016.
- [41] D. Bellaire, O. Großmann, K. Münnemann, H. Hasse: Diffusion coefficients at infinite dilution of carbon dioxide and methane in water, ethanol, cyclohexane, toluene, methanol, and acetone: A PFG-NMR and MD simulation study, The Journal of Chemical Thermodynamics 166 (2022) 106691. DOI: 10.1016/j.jct.2021.106691.
- [42] E. O. Stejskal, J. E. Tanner: Spin diffusion measurements: Spin echoes in the presence of a time-dependent field gradient, The Journal of Chemical Physics 42 (1965) 288–292. DOI: 10.1063/1.1695690.
- [43] H. Hasse: Dampf-Flüssigkeits-Gleichgewichte, Enthalpien und Reaktionskinetik in formaldehydhaltigen Mischungen, Phd thesis, TU Kaiserslautern, 1990.
- [44] L. Rafflenbeul, H. Hartmann: Eine dynamische Apparatur zur Bestimmung von Dampf-Flüssigkeits-Phasengleichgewichten, Chem Technol 7 (1978) 145–148.
- [45] H. Hasse, I. Hahnenstein, G. Maurer: Revised vapor-liquid equilibrium model for multicomponent formaldehyde mixtures, AIChE Journal 36 (1990) 1807–1814. DOI: 10.1002/aic.690361204.
- [46] M. Dyga, A. Keller, H. Hasse: ¹³C-NMR Spectroscopic Study of the Kinetics of Formaldehyde Oligomerization Reactions in the System (Formaldehyde + Water + Isoprenol), Industrial and Engineering Chemistry Research 61 (2022) 224–235. DOI: 10.1021/acs.iecr.1c03911.

- [47] O. Redlich, A. T. Kister: Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Industrial and Engineering Chemistry* 40 (1948) 345–348. DOI: 10.1021/ie50458a036.
- [48] H. Wang, L. Hu, Y. Wu: Excess volumes and partial molar volumes of binary mixtures of 1,2-propanediol carbonate with xylene in the temperature range of (293.15 to 353.15) K, *The Journal of Chemical Thermodynamics* 37 (2005) 1119–1129. DOI: 10.1016/J.JCT.2005.01.017.
- [49] T. Yang, S. Xia, S. Song, X. Fu, P. Ma: Densities and viscosities of N-formylmorpholine (NFM) + p-xylene, + o-xylene, + m-xylene at different temperatures and atmospheric pressure, *Journal of Chemical and Engineering Data* 52 (2007) 2062–2066. DOI: 10.1021/JE7002513.
- [50] M. Behroozi, H. Zarei: Application of the ERAS model to volumetric properties of binary mixtures of banana oil with primary and secondary alcohols (C1–C4) at different temperatures, *The Journal of Chemical Thermodynamics* 43 (2011) 696–704. DOI: 10.1016/J.JCT.2010.12.009.
- [51] A. Jouyban, M. Khoubnasabjafari, Z. Vaez-Gharamaleki, Z. Fekari, W. E. Acree: Calculation of the Viscosity of Binary Liquids at Various Temperatures Using Jouyban–Acree Model, *Chemical and Pharmaceutical Bulletin* 53 (2005) 519–523. DOI: 10.1248/CPB.53.519.
- [52] A. Vignes: Diffusion in Binary Solutions: Variation of Diffusion Coefficient with Composition, *Industrial and Engineering Chemistry Fundamentals* 5 (1966) 189–199. DOI: 10.1021/i160018a007.
- [53] H. Renon, J. M. Prausnitz: Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE Journal* 14 (1968) 135–144. DOI: 10.1002/AIC.690140124.
- [54] B. E. Poling, J. M. Prausnitz, J. P. O’Connell: The properties of gases and liquids, *Chemical engineering*, McGraw-Hill, 2001. DOI: 10.1036/0070116822.
- [55] I. Díaz, M. Rodríguez, E. J. González, M. González-Miquel: A simple and reliable procedure to accurately estimate NRTL interaction parameters from liquid-liquid equilibrium data, *Chemical Engineering Science* 193 (2019) 370–378. DOI: 10.1016/j.ces.2018.09.015.
- [56] D. L. de Klerk, C. E. Schwarz: Simplified Approach to the Parameterization of the NRTL Model for Partially Miscible Binary Systems: $T\tau\tau$ LLE Methodology, *Industrial and Engineering Chemistry Research* 62 (2023) 2021–2035. DOI: 10.1021/acs.iecr.2c03953.

- [57] H. Rachford, J. Rice: Procedure for Use of Electronic Digital Computers in Calculating Flash Vaporization Hydrocarbon Equilibrium, *Journal of Petroleum Technology* 4 (1952) 19–3. DOI: 10.2118/952327-G.
- [58] Y. Teh, G. Rangaiah: A Study of Equation-Solving and Gibbs Free Energy Minimization Methods for Phase Equilibrium Calculations, *Chemical Engineering Research and Design* 80 (2002) 745–759. DOI: 10.1205/026387602320776821.
- [59] T. Specht, H. Hasse, F. Jirasek: Predictive Thermodynamic Modeling of Poorly Specified Mixtures and Applications in Conceptual Fluid Separation Process Design, *Industrial and Engineering Chemistry Research* 62 (2023) 10657–10667. DOI: 10.1021/ACS.IECR.3C01096.
- [60] G. A. Sotiriou, M. Schneider, S. E. Pratsinis: Color-tunable nanophosphors by codoping flame-made Y_2O_3 with Tb and Eu, *Journal of Physical Chemistry C* 115 (2011) 1084–1089. DOI: 10.1021/jp106137u.
- [61] J. Harra, S. Kujanpää, J. Haapanen, P. Juuti, J. M. Mäkelä, L. Hyvärinen, M. Honkanen: Aerosol analysis of residual and nanoparticle fractions from spray pyrolysis of poorly volatile precursors, *AIChE Journal* 63 (2017) 881–892. DOI: 10.1002/aic.15449.
- [62] F. Schneider, S. Suleiman, J. Menser, E. Borukhovich, I. Wlokas, A. Kempf, H. Wiggers, C. Schulz: SpraySyn-A standardized burner configuration for nanoparticle synthesis in spray flames, *Review of Scientific Instruments* 90 (2019) 085108. DOI: 10.1063/1.5090232.
- [63] J. Wei, S. Li, Y. Ren, Y. Zhang, S. D. Tse: Investigating the role of solvent formulations in temperature-controlled liquid-fed aerosol flame synthesis of YAG-based nanoparticles, *Proceedings of the Combustion Institute* 37 (2019) 1193–1201. DOI: 10.1016/j.proci.2018.07.068.
- [64] S. Angel, J. Neises, M. Dreyer, K. Friedel Ortega, M. Behrens, Y. Wang, H. Arandiyán, C. Schulz, H. Wiggers: Spray-flame synthesis of $\text{La}(\text{Fe}, \text{Co})\text{O}_3$ nano-perovskites from metal nitrates, *AIChE Journal* 66 (2020). DOI: 10.1002/aic.16748.
- [65] P. Levene, F. Taylor: On Oxidation of tertiary hydrocarbons, *Journal of Biological Chemistry* 54 (1922) 351–362. DOI: 10.1016/s0021-9258(18)85747-7.
- [66] J. V. Braun, G. Manz: Die Umsetzung von Aldehyden mit Metallen und ihre katalytische Druck-Hydrierung, *Berichte der deutschen chemischen Gesellschaft (A and B Series)* 67 (1934) 1696–1712. DOI: 10.1002/cber.19340671012.

- [67] P. Levene, A. Rothen, G. Meyer: Configurational relationship of members of disubstituted acetic and propionic acids containing an ethyl group, *Journal of Biological Chemistry* 115 (1936) 401–413. DOI: 10.1016/S0021-9258(18)74722-4.
- [68] F. C. Whitmore, J. S. Whitaker, W. A. Mosher, O. N. Breivik, W. R. Wheeler, C. S. Miner, L. H. Sutherland, R. B. Wagner, T. W. Clapper, C. E. Lewis, A. R. Lux, A. H. Popkin: Grignard Reductions. IX. Further studies on the reduction of acid halides, *Journal of the American Chemical Society* 63 (1941) 643–654. DOI: 10.1021/ja01848a004.
- [69] C. Weizmann, M. Sulzbacher, E. Bergmann: Reduction of alpha-beta-unsaturated carbonyl-compounds by sodium-butoxide, *Journal of the Chemical Society* 6 (1947) 851–851.
- [70] C. Weizmann, E. Bergmann, M. Sulzbacher: Further observations on the Guerbet reaction, *Journal of Organic Chemistry* 15 (1950) 54–57.
- [71] W. V. Steele, R. D. Chirico, S. E. Knipmeyer, A. Nguyen: Vapor pressure, heat capacity, and density along the saturation line, measurements for cyclohexanol, 2-cyclohexen-1-one, 1,2-dichloropropane, 1,4-di-tert-butylbenzene, ($\pm$)-2-ethylhexanoic Acid, 2-(methylamino)ethanol, perfluoro-n-heptane, and sulfolan, *Journal of Chemical and Engineering Data* 42 (1997) 1021–1036. DOI: 10.1021/je9701036.
- [72] Y. Shen, Z. Chen, X. Qiu, Z. Ma, H. Li, J. Yang, Y. Ma, J. Gao, Y. Wang: Isobaric vapor–liquid equilibrium measurements and calculations using nontraditional models for the association systems of ethyl acetate + 2-ethylhexanoic acid and propyl acetate + 2-ethylhexanoic acid at atmospheric pressure, *Journal of Chemical and Engineering Data* 65 (2020) 3482–3489. DOI: 10.1021/acs.jced.0c00044.
- [73] Y. Ma, J. Gao, D. Xu, L. Zhang, Y. Wang: Vapor-Liquid equilibrium study of binary mixtures of chloroform, 2-ethylhexanoic acid, and propylene glycol methyl ether at atmospheric pressure, *Journal of Chemical and Engineering Data* 65 (2020) 2271–2279. DOI: 10.1021/ACS.JCED.9B00673.
- [74] G. Stridh: Enthalpy of formation of 2-ethylhexanoic acid, *The Journal of Chemical Thermodynamics* 8 (1976) 193–194.
- [75] E. Andereya, J. D. Chase: The implications of carboxylic acid properties, *Chemical Engineering and Technology* 13 (1990) 304–312. DOI: 10.1002/CEAT.270130141.

- [76] H. Guo, T. W. Smith, P. Iglesias: The study of hexanoate-based protic ionic liquids used as lubricants in steel-steel contact, *Journal of Molecular Liquids* 299 (2020) 112208. DOI: 10.1016/j.molliq.2019.112208.
- [77] A. S. Teja, D. J. Rosenthal: Critical pressures and temperatures of twelve substances using a low residence time flow apparatus, in: *AIChE Symposium Series*, volume 86, 1990, pp. 133–137.
- [78] A. S. Teja, M. J. Anselme: Critical properties of thermally stable and unstable fluids. II. 1986 Results, in: *AIChE Symposium Series*, volume 86, 1990, pp. 115–121.
- [79] L. Qun-Fang, L. Rui-Sen, N. Dan-Yan, H. Yu-Chun: Thermal conductivities of some organic solvents and their binary mixtures, *Journal of Chemical and Engineering Data* 42 (1997) 971–974. DOI: 10.1021/je960351m.
- [80] C. Baroncini, G. Latini, P. Pierpaoli: Thermal conductivity of organic liquid binary mixtures: Measurements and prediction method, *International Journal of Thermophysics* 5 (1984) 387–401. DOI: 10.1007/BF00500868.
- [81] G. Guevara-Carrion, J. Vrabec, H. Hasse: Prediction of self-diffusion coefficient and shear viscosity of water and its binary mixtures with methanol and ethanol by molecular simulation, *The Journal of Chemical Physics* 134 (2011) 074508. DOI: 10.1063/1.3515262.
- [82] D. Ambrose, C. Sprake: Thermodynamic properties of organic oxygen compounds XXV. Vapour pressures and normal boiling temperatures of aliphatic alcohols, *The Journal of Chemical Thermodynamics* 2 (1970) 631–645. DOI: 10.1016/0021-9614(70)90038-8.
- [83] B. Schimmoeller, Y. Jiang, S. E. Pratsinis, A. Baiker: Structure of flame-made vanadia/silica and catalytic behavior in the oxidative dehydrogenation of propane, *Journal of Catalysis* 274 (2010) 64–75. DOI: 10.1016/J.JCAT.2010.06.005.
- [84] T. Boningari, R. Koirala, P. G. Smirniotis: Low-temperature catalytic reduction of NO by NH₃ over vanadia-based nanoparticles prepared by flame-assisted spray pyrolysis: Influence of various supports, *Applied Catalysis B: Environmental* 140–141 (2013) 289–298. DOI: 10.1016/j.apcatb.2013.04.033.
- [85] O. Waser, O. Brenner, A. J. Groehn, S. E. Pratsinis: Process Design for Size-Controlled Flame Spray Synthesis of Li₄Ti₅O₁₂ and Electrochemical Performance, *Chemical and Process Engineering* 38 (2017) 51–66. DOI: 10.1515/cpe-2017-0005.

- [86] C. D. Rosebrock, N. Riefler, T. Wriedt, L. Mädler, S. D. Tse: Disruptive burning of precursor/solvent droplets in flame-spray synthesis of nanoparticles, *AIChE Journal* 59 (2013) 4553–4566. DOI: 10.1002/aic.14234.
- [87] H. Li, S. Pokhrel, M. Schowalter, A. Rosenauer, J. Kiefer, L. Mädler: The gas-phase formation of tin dioxide nanoparticles in single droplet combustion and flame spray pyrolysis, *Combustion and Flame* 215 (2020) 389–400. DOI: 10.1016/j.combustflame.2020.02.004.
- [88] N. M. Garrido, M. Jorge, A. J. Queimada, J. R. B. Gomes, I. G. Economou, E. A. Macedo: Predicting hydration Gibbs energies of alkyl-aromatics using molecular simulation: a comparison of current force fields and the development of a new parameter set for accurate solvation data, *Physical Chemistry Chemical Physics* 13 (2011) 17384. DOI: 10.1039/c1cp21245a.
- [89] A. C. Mengarelli, E. A. Brignole, S. B. Bottini: Activity coefficients of associating mixtures by group contribution, *Fluid Phase Equilibria* 163 (1999) 195–207. DOI: 10.1016/S0378-3812(99)00227-7.
- [90] E. M. Fendu, M. Nicolae, F. Oprea: Vapour-liquid equilibrium for tripropylene glycol + aromatic hydrocarbons binary systems: Measurements and modelling, *Fluid Phase Equilibria* 425 (2016) 188–195. DOI: 10.1016/J.FLUID.2016.05.032.
- [91] R. Raju, K. Prasad: Synthetic applications of 2-ethylhexanoic acid derived reagents, *Tetrahedron* 68 (2012) 1341–1349. DOI: 10.1016/J.TET.2011.10.078.
- [92] A. Labouriau, D. Taylor, T. S. Stephens, M. Pasternak: Mössbauer and NMR characterization of tin octoate: Neat and residues in RTV foams, *Polymer Degradation and Stability* 91 (2006) 1896–1902. DOI: 10.1016/j.polymdegradstab.2005.11.014.
- [93] F. W. van Der Weij: The action of tin compounds in condensation-type RTV silicone rubbers, *Die Makromolekulare Chemie* 181 (1980) 2541–2548. DOI: 10.1002/macp.1980.021811211.
- [94] K. Inyawilert, A. Wisitsoraat, C. Sriprachauwong, A. Tuantranont, S. Phanichphant, C. Liewhiran: Rapid ethanol sensor based on electrolytically-exfoliated graphene-loaded flame-made In-doped SnO₂ composite film, *Sensors and Actuators, B: Chemical* 209 (2015) 40–55. DOI: 10.1016/j.snb.2014.11.086.

- [95] S. Singkammo, A. Wisitsoraat, C. Sriprachuabwong, A. Tuantranont, S. Phanichphant, C. Liewhiran: Electrolytically exfoliated graphene-loaded flame-made Ni-doped SnO₂ composite film for acetone sensing, *ACS Applied Materials and Interfaces* 7 (2015) 3077–3092. DOI: 10.1021/acsami.5b00161.
- [96] N. Tammanoon, A. Wisitsoraat, D. Phokharatkul, A. Tuantranont, S. Phanichphant, V. Yordsri, C. Liewhiran: Highly sensitive acetone sensors based on flame-spray-made La₂O₃-doped SnO₂ nanoparticulate thick films, *Sensors and Actuators B: Chemical* 262 (2018) 245–262. DOI: 10.1016/j.snb.2018.01.238.
- [97] E. R. Tiekink: Structural chemistry of organotin carboxylates: a review of the crystallographic literature, *Applied Organometallic Chemistry* 5 (1991) 1–23. DOI: 10.1002/AOC.590050102.
- [98] A. Doyle, J. Felcman, M. T. d. P. Gambardella, C. N. Verani, M. L. B. Tristão: Anhydrous copper(II) hexanoate from cuprous and cupric oxides. The crystal and molecular structure of Cu₂(O₂CC₅H₁₁)₄, *Polyhedron* 19 (2000) 2621–2627. DOI: 10.1016/S0277-5387(00)00568-4.
- [99] S. Mishra, S. Daniele, L. G. Hubert-Pfalzgraf: Metal 2-ethylhexanoates and related compounds as useful precursors in materials science, *Chemical Society Reviews* 36 (2007) 1770–1787. DOI: 10.1039/B614334M.
- [100] N. Tammanoon, A. Wisitsoraat, C. Sriprachuabwong, D. Phokharatkul, A. Tuantranont, S. Phanichphant, C. Liewhiran: Ultrasensitive NO₂ Sensor Based on Ohmic Metal-Semiconductor Interfaces of Electrolytically Exfoliated Graphene/Flame-Spray-Made SnO₂ Nanoparticles Composite Operating at Low Temperatures, *ACS Applied Materials and Interfaces* 7 (2015) 24338–24352. DOI: 10.1021/acsami.5b09067.
- [101] T. Samerjai, N. Tamaekong, C. Liewhiran, A. Wisitsoraat, A. Tuantranont, S. Phanichphant: Selectivity towards H₂ gas by flame-made Pt-loaded WO₃ sensing films, *Sensors and Actuators, B: Chemical* 157 (2011) 290–297. DOI: 10.1016/j.snb.2011.03.065.
- [102] N. Bloembergen, E. M. Purcell, R. V. Pound: Relaxation effects in nuclear magnetic resonance absorption, *Physical Review* 73 (1948) 679–712. DOI: 10.1103/PhysRev.73.679.
- [103] A. Keller, I. Wloka, M. Kohns, H. Hasse: Solid-liquid equilibria in mixtures of iron(III) nitrate nonahydrate and ethanol or 1-propanol, *Fluid Phase Equilibria* 536 (2021) 112987. DOI: 10.1016/j.fluid.2021.112987.

- [104] H. Li, C. D. Rosebrock, N. Riefler, T. Wriedt, L. Mädler: Experimental investigations on the effects of water vapor and oxygen concentrations in the ambience on the burning constant, lifetime and residuals of single isolated xylene, isobutanol and ethanol droplets, *Experimental Thermal and Fluid Science* 109 (2019). DOI: 10.1016/j.expthermflusci.2019.109920.
- [105] D. F. Othmer, J. Serrano: Solubility Data for Ternary Liquid Systems. Systems of Acetic Acid, Higher Boiling Homologous Acids and Water., *Industrial and Engineering Chemistry* 41 (1949) 1030–1032. DOI: 10.1021/ie50473a033.
- [106] J. G. Stichlmair, H. Klein, S. Rehfeldt: Distillation: principles and practice, John Wiley & Sons, Hoboken, NJ, USA, 2021.
- [107] N. Jüngst, I. Skenderović, B. A. Südholt, G. J. Smallwood, F. E. Kruis, S. A. Kaiser: High-speed imaging and statistics of puffing and micro-exploding droplets in spray-flame synthesis, *Applications in Energy and Combustion Science* 15 (2023) 100167. DOI: 10.1016/j.jaecs.2023.100167.
- [108] M. F. Stodt, J. Kiefer, U. Fritsching: Impact of atomization and spray flow conditions on droplet μ -explosions and temporal self-similarity in the FSP process, *Applications in Energy and Combustion Science* 15 (2023) 100170. DOI: 10.1016/j.jaecs.2023.100170.
- [109] R. L. Brown, S. E. Stein: Boiling Point Data, 2023. DOI: <https://doi.org/10.18434/T4D303>.
- [110] E. Kirschbaum, F. Gerstner: Gleichgewichtskurven, Siede-und Taulinien von Äthylalkohol-Wasser-Gemischen bei Unterdrücken, *Z. VDI, Beihefte Verfahrenstechnik* 1 (1939) 10–15.
- [111] M. Alvina Krähenbühl: Tratamento termodinamico de dados de equilibrio liquido-vapor, Ph.D. thesis, Universidade Estadual de Campinas, Campinas, SP, 1987. DOI: 10.47749/T/UNICAMP.1987.55941.
- [112] K. Iwakabe, H. Kosuge: Isobaric vapor–liquid–liquid equilibria with a newly developed still, *Fluid Phase Equilibria* 192 (2001) 171–186. DOI: 10.1016/S0378-3812(01)00631-8.
- [113] E. C. Voutsas, C. Pamouktsis, D. Argyris, G. D. Pappa: Measurements and thermodynamic modeling of the ethanol–water system with emphasis to the azeotropic region, *Fluid Phase Equilibria* 308 (2011) 135–141. DOI: 10.1016/J.FLUID.2011.06.009.

- [114] J. N. Jaubert, Y. Le Guennec, A. Piña-Martinez, N. Ramirez-Velez, S. Lasala, B. Schmid, I. K. Nikolaidis, I. G. Economou, R. Privat: Benchmark Database Containing Binary-System-High-Quality-Certified Data for Cross-Comparing Thermodynamic Models and Assessing Their Accuracy, *Industrial and Engineering Chemistry Research* 59 (2020) 14981–15027. DOI: 10.1021/ACS.IECR.0C01734.
- [115] T. Magnussen, P. Rasmussen, A. Fredenslund: UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria, *Industrial and Engineering Chemistry Process Design and Development* 20 (1981) 331–339.
- [116] J. Rarey: Extended Flexibility for GE Models and Simultaneous Description of Vapor-Liquid Equilibrium and Liquid-Liquid Equilibrium Using a Nonlinear Transformation of the Concentration Dependence, *Industrial and Engineering Chemistry Research* 44 (2005) 7600–7608. DOI: 10.1021/ie050431w.
- [117] A. Wyczesany: Calculation of vapor-liquid-liquid equilibria at atmospheric and high pressures, *Industrial and Engineering Chemistry Research* 53 (2014) 2509–2519. DOI: 10.1021/IE403418P/SUPPL_FILE/IE403418P_SI_001.PDF.
- [118] E. Forte, A. Kulkarni, J. Burger, M. Bortz, K.-H. Küfer, H. Hasse: Multi-criteria optimization for parametrizing excess Gibbs energy models, *Fluid Phase Equilibria* 522 (2020) 112676. DOI: 10.1016/j.fluid.2020.112676.
- [119] F. Takahashi, I. J. Heilweil, F. L. Dryer: Disruptive Burning Mechanism of Free Slurry Droplets, *Combustion Science and Technology* 65 (1989) 151–165. DOI: 10.1080/00102208908924046.
- [120] I. Skenderović, G. Kotalczyk, F. Kruis: Dual Population Balance Monte Carlo Simulation of Particle Synthesis by Flame Spray Pyrolysis, *Processes* 6 (2018) 253. DOI: 10.3390/pr6120253.
- [121] G. Faeth: Current status of droplet and liquid combustion, *Progress in Energy and Combustion Science* 3 (1977) 191–224. DOI: 10.1016/0360-1285(77)90012-0.
- [122] W. A. Sirignano: Fuel droplet vaporization and spray combustion theory, *Progress in Energy and Combustion Science* 9 (1983) 291–322. DOI: 10.1016/0360-1285(83)90011-4.
- [123] B. Abramzon, W. Sirignano: Droplet vaporization model for spray combustion calculations, *International Journal of Heat and Mass Transfer* 32 (1989) 1605–1618. DOI: 10.1016/0017-9310(89)90043-4.

- [124] J. Tamim, W. Hallett: A continuous thermodynamics model for multicomponent droplet vaporization, *Chemical Engineering Science* 50 (1995) 2933–2942. DOI: 10.1016/0009-2509(95)00131-N.
- [125] S. S. Sazhin: Advanced models of fuel droplet heating and evaporation, *Progress in Energy and Combustion Science* 32 (2006) 162–214. DOI: 10.1016/j.pecs.2005.11.001.
- [126] S. S. Sazhin: Modelling of fuel droplet heating and evaporation: Recent results and unsolved problems, *Fuel* 196 (2017) 69–101. DOI: 10.1016/j.fuel.2017.01.048.
- [127] M. C. Heine, S. E. Pratsinis: Droplet and particle dynamics during flame spray synthesis of nanoparticles, *Industrial and Engineering Chemistry Research* 44 (2005) 6222–6232. DOI: 10.1021/ie0490278.
- [128] A. J. Gröhn, S. E. Pratsinis, K. Wegner: Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO_2 , *Chemical Engineering Journal* 191 (2012) 491–502. DOI: 10.1016/j.cej.2012.02.093.
- [129] P. Narasu, A. Keller, M. Kohns, H. Hasse, E. Gutheil: Numerical study of the evaporation and thermal decomposition of a single iron(III) nitrate non-hydrate/ethanol droplet, *International Journal of Thermal Sciences* 170 (2021) 107133. DOI: 10.1016/j.ijthermalsci.2021.107133.
- [130] P. Narasu, M. Nanjaiah, I. Wlokas, E. Gutheil: Numerical simulation and parameterization of the heating and evaporation of a titanium (IV) isopropoxide/p-xylene precursor/solvent droplet in hot convective air, *International Journal of Multiphase Flow* 150 (2022) 104006. DOI: 10.1016/j.ijmultiphaseflow.2022.104006.
- [131] P. Narasu, E. Gutheil: A new model for puffing and micro-explosion of single titanium(IV) isopropoxide/p-xylene precursor solution droplets, *International Journal of Heat and Mass Transfer* 202 (2023) 123647. DOI: 10.1016/j.ijheatmasstransfer.2022.123647.
- [132] M. Najimu, V. Baghdassarian, S. Leask, V. McDonell, B. Padak, E. Sasmaz: Incorporation of film theory in single droplet combustion model for prediction of precursor release in flame spray pyrolysis, *Proceedings of the Combustion Institute* 000 (2023) 1–11. DOI: 10.1016/j.proci.2022.12.001.
- [133] H. Q. Zhang, C. K. Law: Effects of temporally varying liquid-phase mass diffusivity in multicomponent droplet gasification, *Combustion and Flame* 153 (2008) 593–602. DOI: 10.1016/j.combustflame.2007.12.007.

- [134] G. Brenn, L. J. Deviprasath, F. Durst, C. Fink: Evaporation of acoustically levitated multi-component liquid droplets, *International Journal of Heat and Mass Transfer* 50 (2007) 5073–5086. DOI: 10.1016/j.ijheatmasstransfer.2007.07.036.
- [135] M. Gonchikzhapov, T. Kasper: Decomposition reactions of $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and TTIP as precursors for the spray-flame synthesis of nanoparticles in partial spray evaporation at low temperatures, *Industrial and Engineering Chemistry Research* 59 (2020) 8551–8561. DOI: 10.1021/acs.iecr.9b06667.
- [136] R. Kneer, M. Schneider, B. Noll, S. Wittig: Diffusion controlled evaporation of a multicomponent droplet: theoretical studies on the importance of variable liquid properties, *International Journal of Heat and Mass Transfer* 36 (1993) 2403–2415. DOI: 10.1016/S0017-9310(05)80124-3.
- [137] VDI (Ed.): VDI-Wärmeatlas, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013. DOI: 10.1007/978-3-642-19981-3.
- [138] F. J. Zeleznik: A General IBM 704 Or 7090 Computer Program for Computation of Chemical Equilibrium Compositions, Rocket Performance, and Chapman-Jouguet Detonations: Frank J. Zeleznik and Sanford Gordon, National Aeronautics and Space Administration, 1962.
- [139] P. Buerger, D. Nurkowski, J. Akroyd, M. Kraft: A kinetic mechanism for the thermal decomposition of titanium tetraisopropoxide, *Proceedings of the Combustion Institute* 36 (2017) 1019–1027. DOI: 10.1016/j.proci.2016.08.062.
- [140] J. A. Draeger, D. W. Scott: Ideal gas thermodynamic properties of 1,4-dimethylbenzene, *The Journal of Chemical Physics* 74 (1981) 4748–4749. DOI: 10.1063/1.441629.
- [141] F. J. Martins, J. Kirchmann, A. Kronenburg, F. Beyrau: Experimental investigation of axisymmetric, turbulent, annular jets discharged through the nozzle of the SPP1980 SpraySyn burner under isothermal and reacting conditions, *Experimental Thermal and Fluid Science* 114 (2020) 110052. DOI: 10.1016/j.expthermflusci.2020.110052.
- [142] S. N. R. Inturi, T. Boningari, M. Suidan, P. G. Smirniotis: Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO_2 , *Applied Catalysis B: Environmental* 144 (2014) 333–342. DOI: 10.1016/j.apcatb.2013.07.032.

- [143] C. Liu, S. Li, Y. Zong, Q. Yao, S. D. Tse: Laser-based investigation of the transition from droplets to nanoparticles in flame-assisted spray synthesis of functional nanoparticles, *Proceedings of the Combustion Institute* 36 (2017) 1109–1117. DOI: 10.1016/j.proci.2016.06.166.
- [144] F. Pan, H. Lin, H. Zhai, Z. Miao, Y. Zhang, K. Xu, B. Guan, H. Huang, H. Zhang: Pd-doped TiO₂ film sensors prepared by premixed stagnation flames for CO and NH₃ gas sensing, *Sensors and Actuators, B: Chemical* 261 (2018) 451–459. DOI: 10.1016/j.snb.2018.01.173.
- [145] X. Yang, J. Wang, Y. Fang: Volumetric and viscosity properties of binary mixtures containing asymmetrical Gemini ionic liquid, *Huagong Xuebao/CIESC Journal* 70 (2019) 4131–4142. DOI: 10.11949/0438-1157.20190470.
- [146] K. S. Kim, B. H. Park: Volumetric properties of solutions of choline chloride and glycerol deep eutectic solvent with water, methanol, ethanol, or iso-propanol, *Journal of Molecular Liquids* 254 (2018) 272–279. DOI: 10.1016/J.MOLLIQ.2018.01.087.
- [147] M. S. Alam, B. Ashokkumar, A. Mohammed Siddiq: The density, dynamic viscosity and kinematic viscosity of protic polar solvents (pure and mixed systems) studies: A theoretical insight of thermophysical properties, *Journal of Molecular Liquids* 251 (2018) 458–469. DOI: 10.1016/J.MOLLIQ.2017.12.089.
- [148] L. Zhang, X. Lu, D. Ye, Y. Guo, W. Fang: Density and Viscosity for Binary Mixtures of the Ionic Liquid 2,2-Diethyl-1,1,3,3-Tetramethylguanidinium Ethyl Sulfate with Water, Methanol, or Ethanol, *Journal of Chemical and Engineering Data* 61 (2016) 1023–1031. DOI: 10.1021/ACS.JCED.5B00365.
- [149] X. Lu, D. Wu, D. Ye, Y. Wang, Y. Guo, W. Fang: Densities and Viscosities of Binary Mixtures of 2-Ethyl-1,1,3,3-tetramethylguanidinium Ionic Liquids with Ethanol and 1-Propanol, *Journal of Chemical and Engineering Data* 60 (2015) 2618–2628. DOI: 10.1021/ACS.JCED.5B00259.
- [150] J. M. Vuksanović, I. R. Radović, S. P. Šerbanović, M. L. Kijevčanin: Experimental study of the thermodynamic and transport properties of binary mixtures of poly(ethylene glycol) diacrylate and alcohols at different temperatures, *Journal of the Serbian Chemical Society* 80 (2015) 933–946. DOI: 10.2298/JSC141009005V.
- [151] Q. Cao, X. Lu, X. Wu, Y. Guo, L. Xu, W. Fang: Density, viscosity, and conductivity of binary mixtures of the ionic liquid N -(2-hydroxyethyl)piperazinium

- propionate with water, methanol, or ethanol, *Journal of Chemical and Engineering Data* 60 (2015) 455–463. DOI: 10.1021/JE500380X.
- [152] C. Zhu, S. Han, J. Liu, Y. Ma: Densities and viscosities of diaminotoluene with water, ethanol, propan-1-ol, and butan-1-ol from (293.15 to 333.15) K, *Journal of Chemical and Engineering Data* 59 (2014) 880–889. DOI: 10.1021/JE400968V.
- [153] J. J. Cano-Gómez, G. A. Iglesias-Silva, M. Ramos-Estrada, K. R. Hall: Densities and viscosities for binary liquid mixtures of ethanol + 1-propanol, 1-butanol, and 1-pentanol from (293.15 to 328.15) K at 0.1 MPa, *Journal of Chemical and Engineering Data* 57 (2012) 2560–2567. DOI: 10.1021/JE300632P.
- [154] Y. H. Gong, C. Shen, Y. Z. Lu, H. Meng, C. X. Li: Viscosity and density measurements for six binary mixtures of water (methanol or ethanol) with an ionic liquid ([BMIM][DMP] or [EMIM][DMP]) at atmospheric pressure in the temperature range of (293.15 to 333.15) K, *Journal of Chemical and Engineering Data* 57 (2012) 33–39. DOI: 10.1021/JE200600P.
- [155] K. A. Kurnia, M. I. Mutalib, T. Murugesan, B. Ariwahjoedi: Physico-chemical Properties of Binary Mixtures of the Protic Ionic Liquid Bis(2-hydroxyethyl)methylammonium Formate with Methanol, Ethanol, and 1-Propanol, *Journal of Solution Chemistry* 2011 40:5 40 (2011) 818–831. DOI: 10.1007/S10953-011-9680-8.
- [156] F. A. Goncalves, A. R. Trindade, C. S. Costa, J. C. Bernardo, I. Johnson, I. M. Fonseca, A. G. Ferreira: PVT, viscosity, and surface tension of ethanol: New measurements and literature data evaluation, *The Journal of Chemical Thermodynamics* 42 (2010) 1039–1049. DOI: 10.1016/J.JCT.2010.03.022.
- [157] D. Matkowska, A. Gołdon, T. Hofman: Densities, excess volumes, isobaric expansivities, and isothermal compressibilities of the 1-ethyl-3-methylimidazolium ethylsulfate + ethanol system at temperatures (283.15 to 343.15) K and pressures from (0.1 to 35) MPa, *Journal of Chemical and Engineering Data* 55 (2010) 685–693. DOI: 10.1021/JE900414P.
- [158] R. Gonzalez-Olmos, M. Iglesias, S. Mattedi: Influence of temperature on thermodynamics of ethanol + hydrocarbon gasoline additives, *Physics and Chemistry of Liquids* 48 (2010) 337–384. DOI: 10.1080/00319100902894223.
- [159] C. K. Zéberg-Mikkelsen, L. Lugo, J. García, J. Fernández: Volumetric properties under pressure for the binary system ethanol + toluene, *Fluid Phase Equilibria* 235 (2005) 139–151. DOI: 10.1016/J.FLUID.2005.05.023.

- [160] G. Slvarampraead, M. Venkateahwara Rao, D. H. L Prasad: Density and Viscosity of Density and viscosity measurements on the binary mixtures of ethanol, *J. Chem. Eng. Data* 35 (1990) 122–124.
- [161] G. Watson, C. K. Zéberg-Mikkelsen, A. Baylaucq, C. Boned: High-pressure density measurements for the binary system ethanol + heptane, *Journal of Chemical and Engineering Data* 51 (2006) 112–118. DOI: 10.1021/JE050261U.
- [162] M. B. Silveira, F. R. Do Carmo, R. S. Santiago-Aguiar, H. B. De Sant’Ana: Ab–diesel: Liquid–liquid equilibrium and volumetric transport properties, *Fuel* 119 (2014) 292–300. DOI: 10.1016/J.FUEL.2013.11.022.
- [163] A. Estrada-Baltazar, G. A. Iglesias-Silva, C. Caballero-Cerón: Volumetric and transport properties of binary mixtures of n -octane + ethanol, + 1-propanol, + 1-butanol, and + 1-pentanol from (293.15 to 323.15) K at atmospheric pressure, *Journal of Chemical and Engineering Data* 58 (2013) 3351–3363. DOI: 10.1021/JE4004806.
- [164] M. Anouti, J. Jacquemin, D. Lemordant: Volumetric properties, viscosities, and isobaric heat capacities of imidazolium octanoate protic ionic liquid in molecular solvents, *Journal of Chemical and Engineering Data* 55 (2010) 5719–5728. DOI: 10.1021/JE100671V.
- [165] V. N. Popov, B. A. Malov: Thermal conductivity of ethanol-water system in temperature range 20–300 degrees C and at pressures up to 30 MN/m², *Thermal Engineering* 18 (1971) 125.
- [166] H. L. Mason: Thermal Conductivity of Some Industrial Liquids From 0 to 100 C, *Journal of Fluids Engineering* 76 (1954) 817–820. DOI: 10.1115/1.4014979.
- [167] H. Poltz, R. Jugel: Die Wärmeleitfähigkeit von Alkoholen, *Wärme- und Stoffübertragung* 1 (1968) 197–201. DOI: 10.1007/BF00763896.
- [168] C. Zheng, Y. Gao: New Thermal Conductivity Equations for Pure Liquids and Liquid Mixtures, in: *Thermal conductivity* 19, Cookeville, Tennessee, 1988, pp. 317–327.
- [169] O. K. Bates, G. Hazzard, G. Palmer: Thermal Conductivity of Liquids: Binary Mixtures of Water-Methyl Alcohol and Water-Ethyl Alcohol, *Industrial and Engineering Chemistry - Analytical Edition* 10 (1938) 314–318. DOI: 10.1021/AC50122A006.
- [170] X. Cui, H. Zhu, C. H. He, K. J. Wu: Measurement of the Thermal Conductivity of 1-Butyl-3-methylimidazolium l -Tryptophan + Water + Ethanol Mixtures at

- T = (283.15 to 333.15) K, *Journal of Chemical and Engineering Data* 64 (2019) 1586–1593. DOI: 10.1021/ACS.JCED.8B01147.
- [171] Q. L. Chen, K. J. Wu, C. H. He: Thermal conductivities of [EMIM][EtSO₄], [EMIM][EtSO₄] + C₂H₅OH, [EMIM][EtSO₄] + H₂O, and [EMIM][EtSO₄] + C₂H₅OH + H₂O at T = (283.15 to 343.15) K, *Journal of Chemical and Engineering Data* 58 (2013) 2058–2064. DOI: 10.1021/JE400268T.
- [172] R. Tufeu, B. Le Neindre, P. Bury, P. Johannin: Mesure de la conductibilité thermique de quelques liquides, *Revue Gén. Thermique* 76 (1968) 365–377.
- [173] G. M. Mallan, M. S. Michaelian, F. J. Lockhart: Liquid thermal conductivities of organic compounds and petroleum fractions, *Journal of Chemical and Engineering Data* 17 (1972) 412–415.
- [174] J. E. S. Venart, C. Krishnamurthy: The thermal conductivity of pure organic liquids, in: *Proceedings of the 7th conference on thermal conductivity* (Special Publication 302, NBS, Gaithersburg, MD, 1968), 1968, pp. 659–670.
- [175] A. R. Challoner, H. A. Gundry, R. W. Powell: A radial heat-flow apparatus for liquid thermal conductivity determinations, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 245 (1958) 259–267. DOI: 10.1098/rspa.1958.0081.
- [176] J. D. Raal, R. L. Rljsdljk: Measurement of Alcohol Thermal Conductivities Using a Relative Strain-Compensated Hot-Wire Method, *J. Chem. Eng. Data* 26 (1981) 351–359.
- [177] J. C. Zhou, Y. Y. Che, K. J. Wu, J. Shen, C. H. He: Thermal conductivity of DMSO + C₂H₅OH, DMSO + H₂O, and DMSO + C₂H₅OH + H₂O mixtures at T = (278.15 to 338.15) K, *Journal of Chemical and Engineering Data* 58 (2013) 663–670. DOI: 10.1021/JE301171Y.
- [178] J. Peleteiro, J. Troncoso, D. González-Salgado, J. L. Valencia, C. A. Cerdeiriña, L. Román: Anomalous Excess Heat Capacities of Ethanol + Alkane Mixtures, *International Journal of Thermophysics* 2004 25:3 25 (2004) 787–803. DOI: 10.1023/B:IJOT.0000034237.54486.BB.
- [179] I. Rabinovich, P. N. Nikolaev: Isotope effect in the specific heat of certain deuterium compounds, in: *Doklady Akademii Nauk*, volume 142, Russian Academy of Sciences, 1962, pp. 1335–1338.

- [180] I. Klesper: Messung der spezifischen Wärmen binärer Flüssigkeitsgemische, *Zeitschrift für Physikalische Chemie* 51 (1966) 1–12. DOI: 10.1524/ZPCH.1966.51.1_2.001.
- [181] Y. Zheng, Z. Wei, X. Song: Measurements of isobaric heat capacities for HFE-7000 and HFE-7100 at different temperatures and pressures, *Fluid Phase Equilibria* 425 (2016) 335–341. DOI: 10.1016/J.FLUID.2016.06.024.
- [182] S. L. Rivkin, A. N. Vinnikova: Specific heat of ethyl alcohol solutions in water at temperatures of 25–50° C, *Teploenergetika* (1964) 59–63.
- [183] J. F. Martínez-López, S. Schneider, D. Salavera, A. M. Mainar, J. S. Urieta, J. I. Pardo: Molar heat capacities of the mixture 1,8-cineole + ethanol at several temperatures and atmospheric pressure, *The Journal of Chemical Thermodynamics* 92 (2016) 146–151. DOI: 10.1016/J.JCT.2015.09.012.
- [184] E. F. Fiock, D. C. Ginnings, W. B. Holton: Calorimetric determinations of thermal properties of methyl alcohol, ethyl alcohol, and benzene, *J. Res. Natl. Bur. Stand* 6 (1931) 881–900.
- [185] N. Karger, T. Vardag, H. D. Lüdemann: Temperature dependence of self-diffusion in compressed monohydric alcohols, *The Journal of Chemical Physics* 93 (1990) 3437–3444. DOI: 10.1063/1.458825.
- [186] K. C. Pratt, W. A. Wakeham: Self-diffusion in water and monohydric alcohols, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* 73 (1977) 997–1002. DOI: 10.1039/F29777300997.
- [187] R. E. Rathbun, A. L. Babb: Self-diffusion in liquids. III. Temperature dependence in pure liquids 1, *The Journal of Physical Chemistry* 65 (1961) 1072–1074. DOI: 10.1021/j100824a520.
- [188] K. Graupner, E. R. Winter: Some measurements of the self-diffusion coefficients of liquids, *Journal of the Chemical Society (Resumed)* 63 (1952) 1145–1150. DOI: 10.1039/jr9520001145.
- [189] J. R. Partington, R. F. Hudson, K. W. Bagnall: L’auto-diffusion d’une série d’alcools aliphatiques, *Journal de Chimie Physique* 55 (1958) 77–82. DOI: 10.1051/jcp/1958550077.
- [190] H. Chen, H. Fang, Y. Chen, S. C. N. Hsu, Y. Lai, H. Ou, W. Peng, Y. Chang, Y. Tsou, T. Wu, H. Chung, Y. Chen, T. C. Huang, B. S. Wu: In situ formation of

Sn(IV) catalyst with increased activity in ϵ -caprolactone and L-lactide polymerization using stannous(II) 2-ethylhexanoate, *Journal of Polymer Science Part A: Polymer Chemistry* 50 (2012) 3286–3294. DOI: 10.1002/pola.26108.

A Supporting Information for Chapter 4

A.1 Comparison of Experimental Pure Component Properties to Literature Data

Relative deviations are calculated between the measured data from Chapter 4 as well as from the literature and the results of the empirical correlations from the main text. Since the procedure is exactly the same for the density, viscosity, thermal conductivity, and isobaric heat capacity, it is shown here using the exemplary property z :

$$\Delta_{\text{rel}} z = \frac{z^{\text{exp}} - z^{\text{fit}}}{z^{\text{fit}}}$$

A.1.1 Results for Pure EHA

Figure A.1 shows the experimental results from Chapter 4 for the density of pure EHA in comparison with experimental data from the literature. Since there are only two data points at atmospheric pressure from the literature, a deviation plot is not shown in this case. Table A.1 lists the experimental results for the viscosity of pure EHA. Figure A.2 shows the experimental results from Chapter 4 for the viscosity of pure EHA in comparison with experimental data from the literature. Again, a deviation plot is not shown because there are only two relevant data points for the comparison. Reasonable agreement is found but deviations increase with increasing temperature.

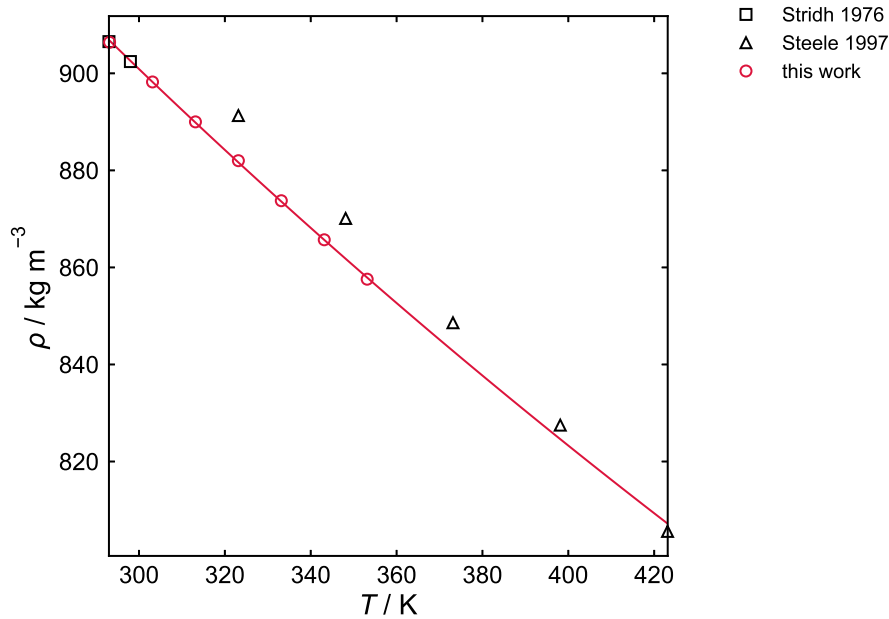


Figure A.1: Density of pure EHA at 101.3 kPa (data from Chapter 4 and data from Stridh [74]) or along the saturation line (data from Steele et al. [71]) as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [71, 74] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

Table A.1: Viscosity η of pure EHA at different temperatures T and $p = 101.3$ kPa. The combined expanded uncertainties are given in the table for $U(\eta)$, $u(p) = 3$ kPa and $u(T) = 0.05$ K. Results for 293.15 to 333.15 K are repeated here for convenience. Results for 343.15 and 353.15 K are not shown in the main manuscript.

T / K	$\eta / \text{mPa s}$ ($U(\eta) / \text{mPa s}$)
293.15	7.529 (0.146)
303.15	5.354 (0.046)
313.15	3.961 (0.034)
323.15	3.042 (0.026)
333.15	2.413 (0.021)
343.15	1.961 (0.017)
353.15	1.629 (0.014)

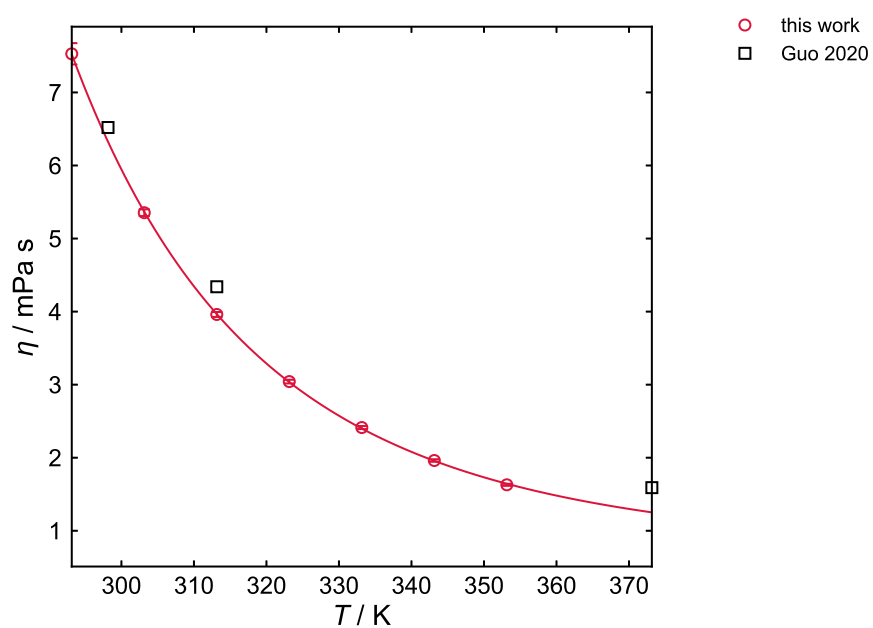


Figure A.2: Viscosity of pure EHA at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [76] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

A.1.2 Results for Pure Ethanol

Figures A.3 to A.10 show the experimental results for the density, viscosity, thermal conductivity and isobaric heat capacity of pure ethanol in comparison with literature values.

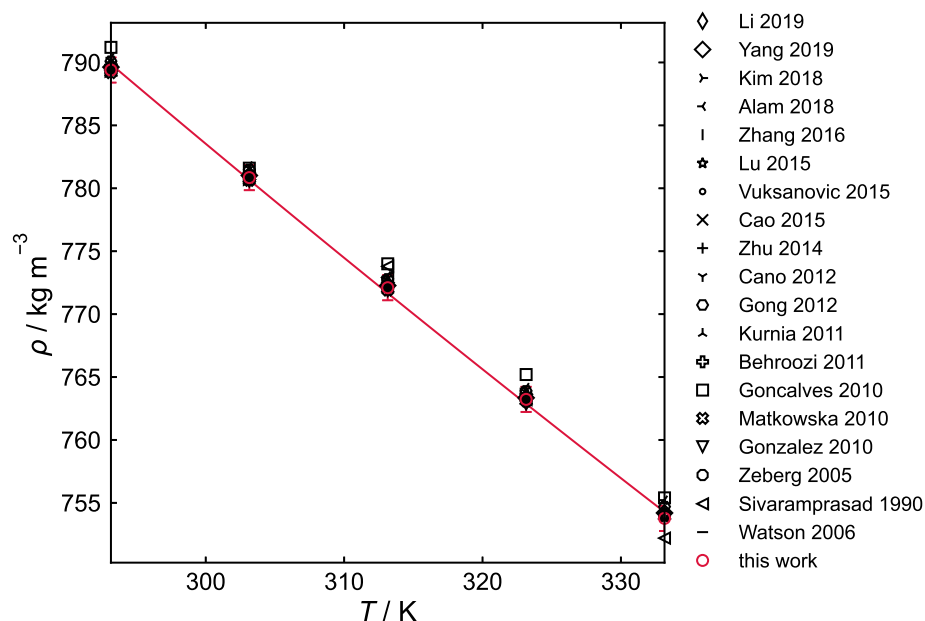


Figure A.3: Density of pure ethanol at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [27, 50, 145–161] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

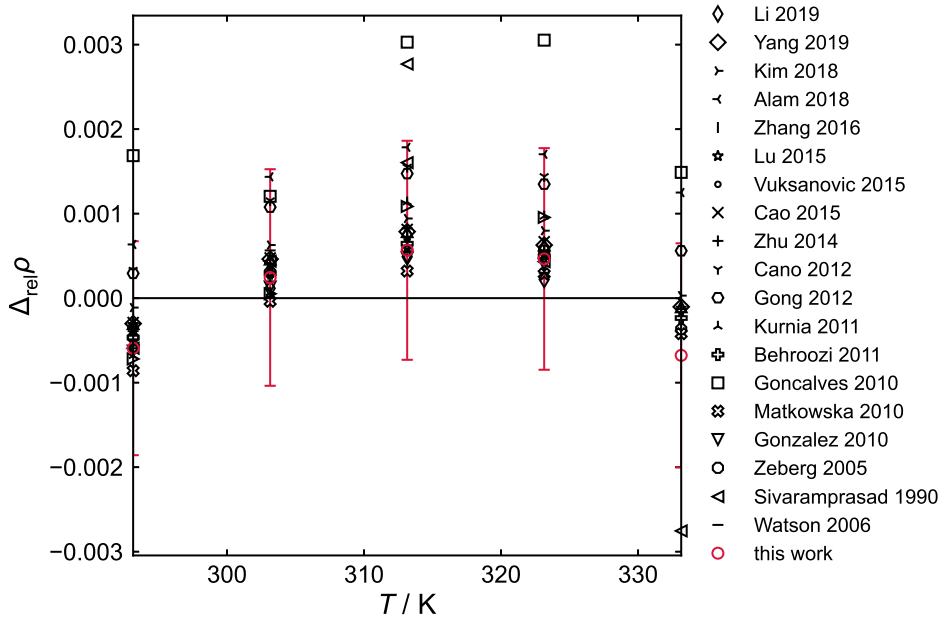


Figure A.4: Relative deviation between experimental densities of pure ethanol from Chapter 4 or literature [27, 50, 145–161] as denoted in the legend and the fit to the data from Chapter 4 as described there.

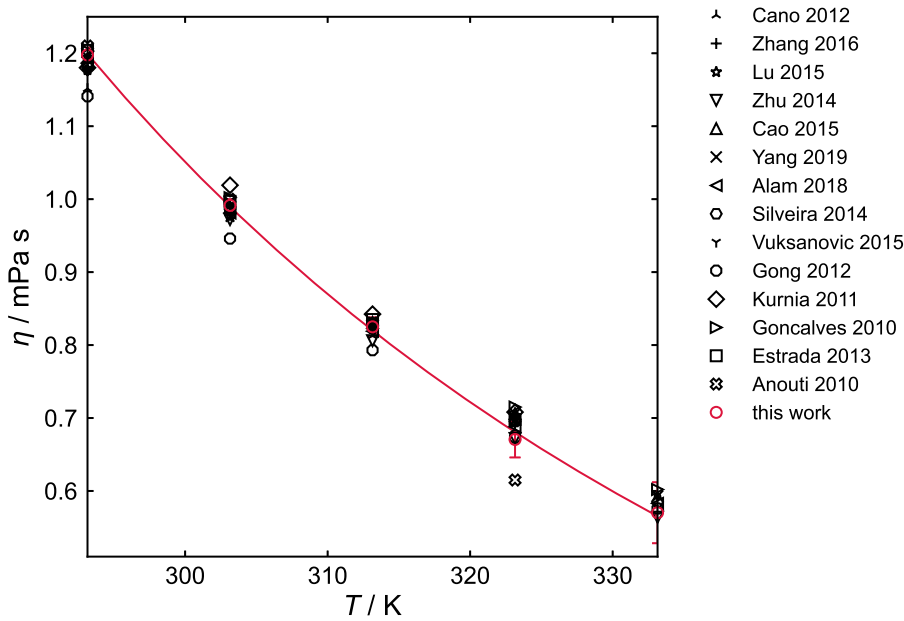


Figure A.5: Viscosity of pure ethanol at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [145, 147–156, 162–164] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

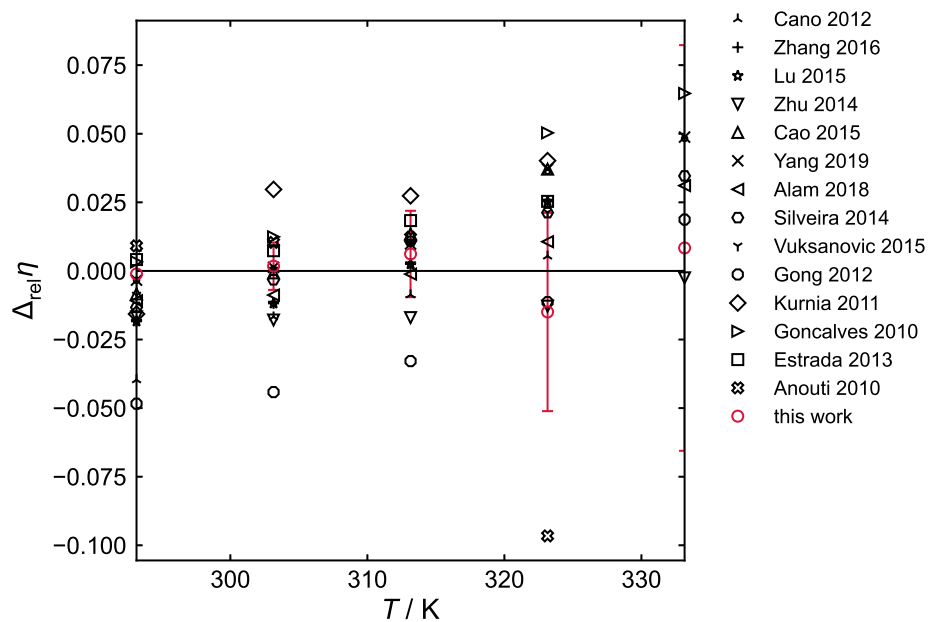


Figure A.6: Relative deviation between experimental viscosities of pure ethanol from Chapter 4 or literature [145, 147–156, 162–164] as denoted in the legend and the fit to the data from Chapter 4 as described in the main text.

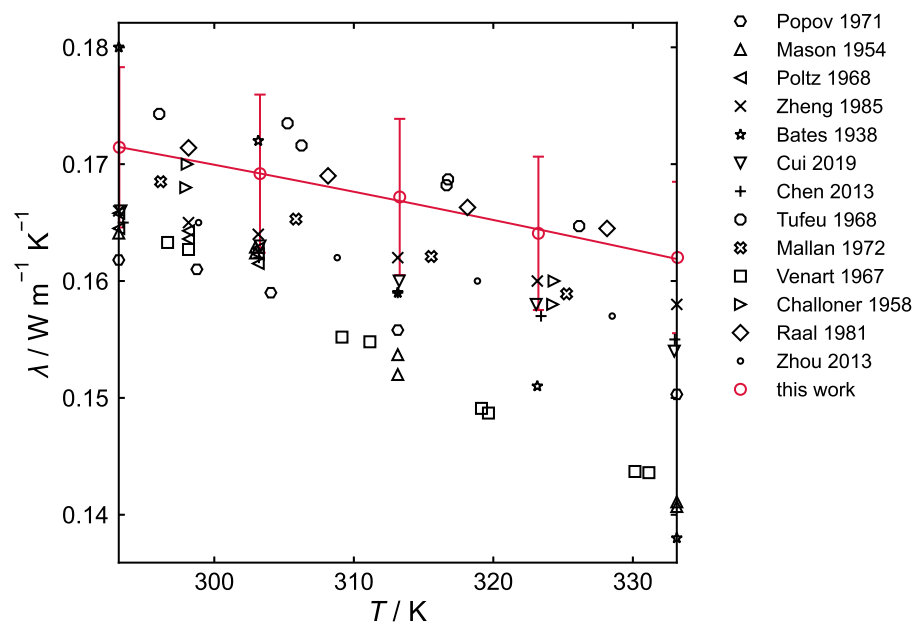


Figure A.7: Thermal conductivity of pure ethanol at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [165–177] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

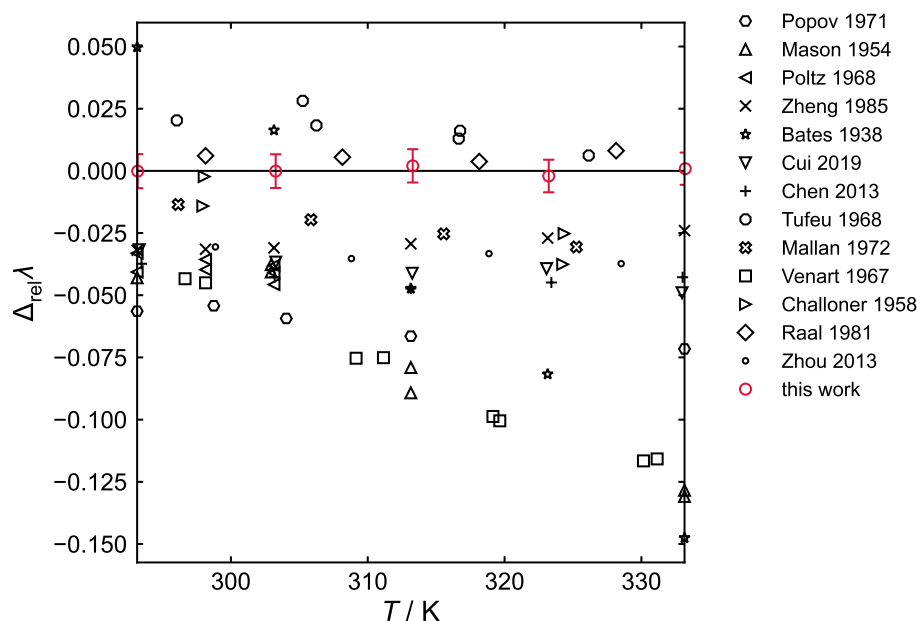


Figure A.8: Relative deviation between experimental thermal conductivities of pure ethanol from Chapter 4 or literature [165–177] as denoted in the legend and the fit to the data from Chapter 4 as described in the main text.

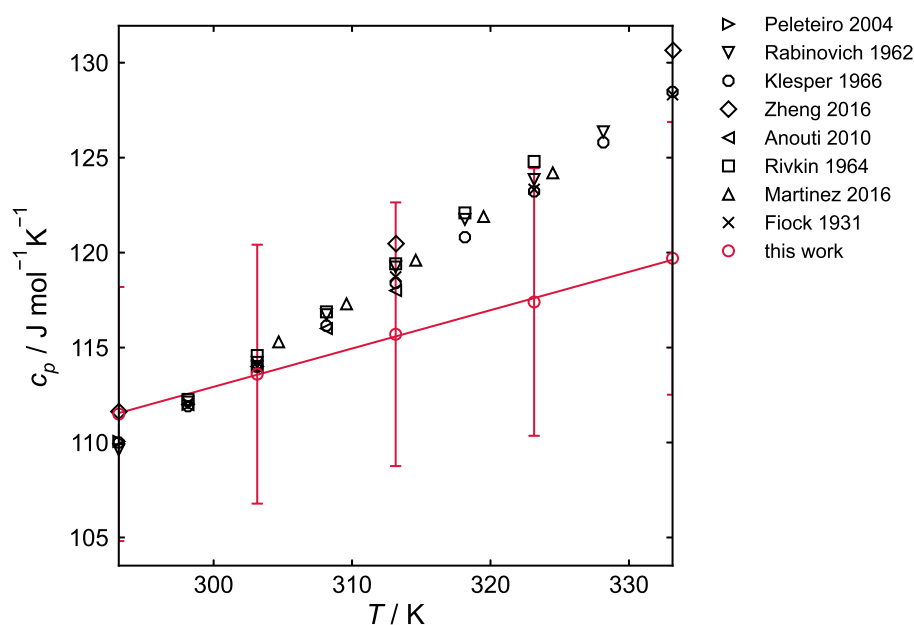


Figure A.9: Isobaric heat capacity of pure ethanol at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [164, 178–184] as denoted in the legend. The line denotes the fit of the data from Chapter 4 as described there.

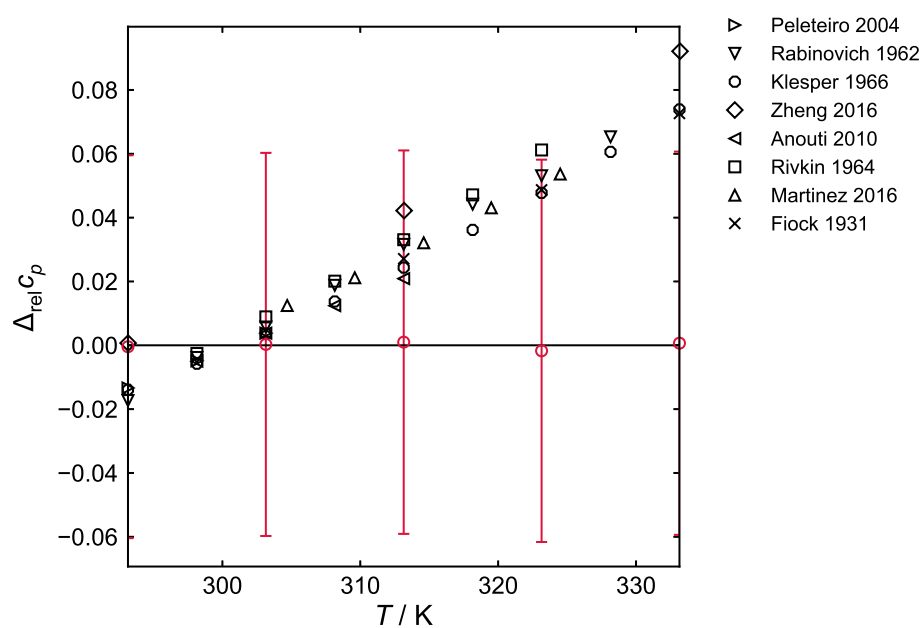


Figure A.10: Relative deviation between experimental isobaric heat capacities of pure ethanol from Chapter 4 or literature [164, 178–184] as denoted in the legend and the fit to the data from Chapter 4 as described in the main text.

A.2 Self-Diffusion Coefficients of the Pure Components

A.2.1 EHA

Table A.2 gives the experimental results for the self-diffusion coefficient of pure EHA at 101.3 kPa and temperatures between 298.15 and 353.15 K. Additionally, the results are depicted in Figure A.11.

Table A.2: Self-diffusion coefficient D_{EHA} and temperature T at $p = 101.3$ kPa. The combined expanded uncertainty of the self-diffusion coefficient of EHA is $U(D_{\text{EHA}})$ ($k = 2$) = $10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $u(T) = 0.1$ K and $u(p) = 3$ kPa.

T / K	$D_{\text{EHA}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$
298.15	0.126
303.15	0.152
313.15	0.213
323.15	0.287
333.15	0.375
343.15	0.477
353.15	0.596

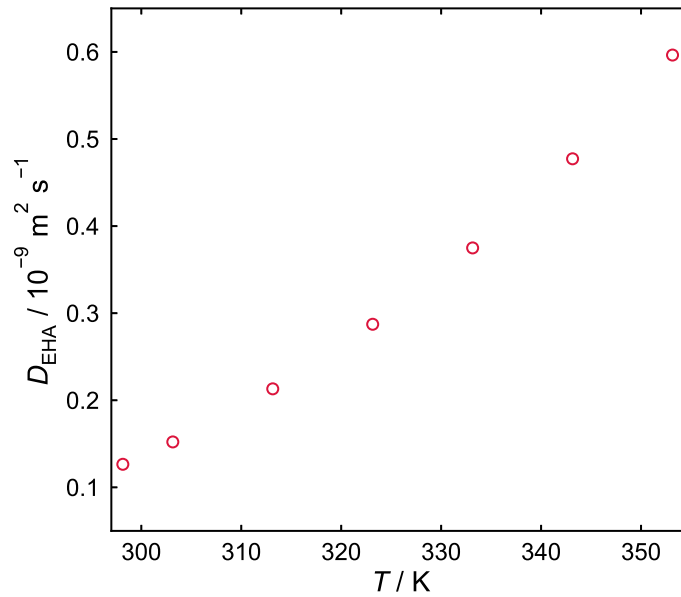


Figure A.11: Self-diffusion coefficient of pure EHA at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4. Error bars are within symbol size.

A.2.2 Ethanol

The results of the self-diffusion coefficient measurements of pure ethanol at 101.3 kPa and temperatures between 298.15 and 333.15 K are given in Table A.3. As evident from Figure A.12, the results from Chapter 4 for the self-diffusion coefficient of pure ethanol are in excellent agreement with literature data.

Table A.3: Self-diffusion coefficient D_{EtOH} and temperature T at $p = 101.3$ kPa. The combined expanded uncertainties of the self-diffusion coefficient $U(D_{\text{EtOH}})$ ($k = 2$) are given in the table and $u(T) = 0.1$ K and $u(p) = 3$ kPa.

T / K	$D_{\text{EtOH}} / 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ($U(D_{\text{EtOH}}) / 10^{-9} \text{ m}^2 \text{ s}^{-1}$)
298.15	1.071 (0.001)
303.15	1.199 (0.002)
313.15	1.494 (0.002)
323.15	1.843 (0.007)
333.15	2.251 (0.003)

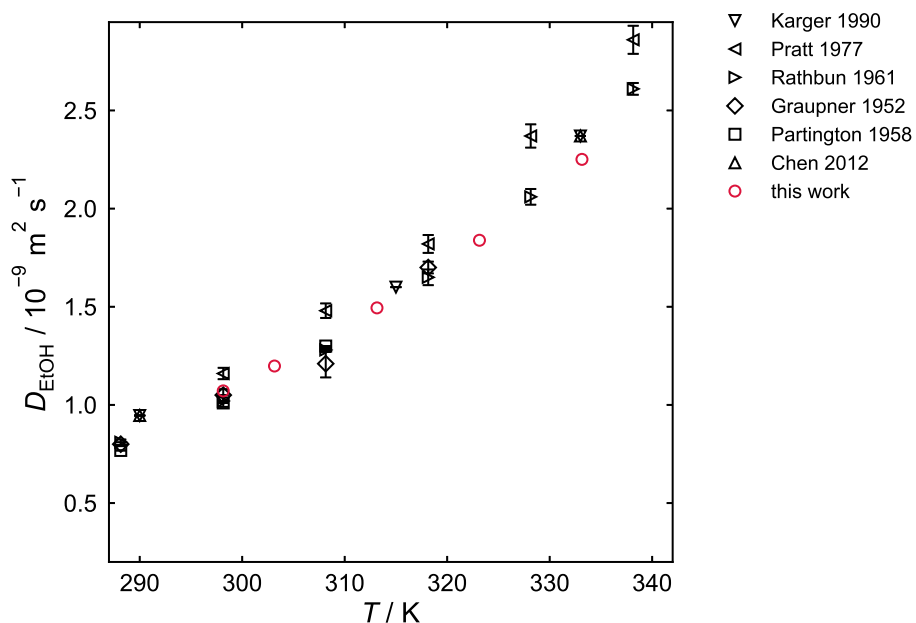


Figure A.12: Self-diffusion coefficient of pure ethanol at 101.3 kPa as a function of temperature. Symbols are experimental results from Chapter 4 and measurement data from the literature [185–190] as denoted in the insert legend. Error bars are with symbol size.

B Supporting Information for Chapter 5

Figure B.1 shows the experimental results for the molar volume together with the correlation results. The molar volume decreases with decreasing temperature and increasing *p*-xylene mole fraction. The almost perfectly linear dependence on the molar composition indicates an approximately ideal behavior of this property.

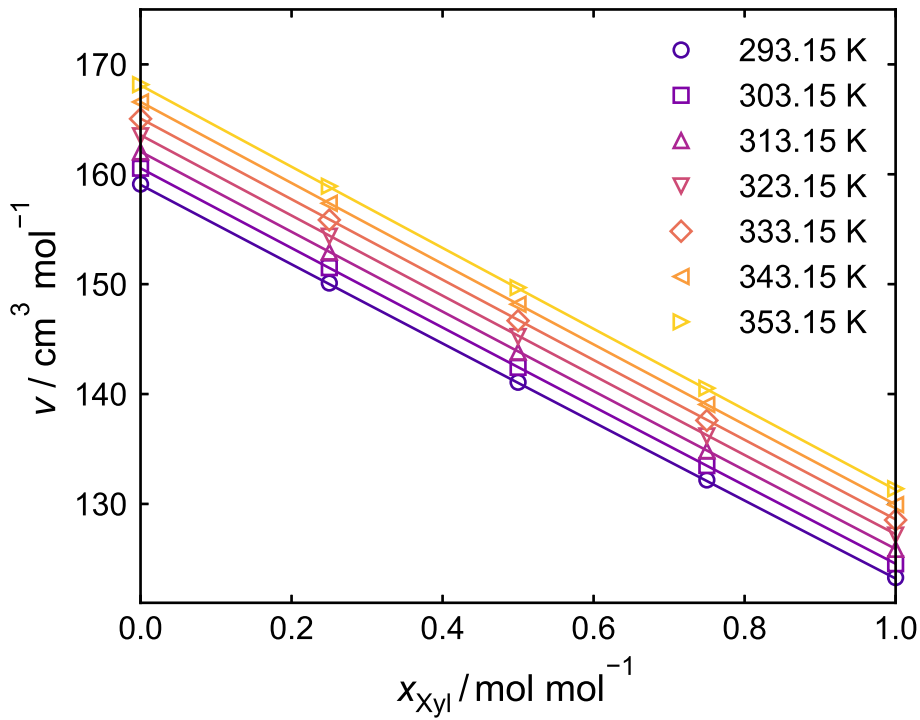


Figure B.1: Molar volume v of mixtures of EHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Experimental uncertainties are within symbol size. Lines are empirical correlations (cf. Eqs. (5) – (9)) with parameters listed in Tables 21 and 22.

C Supporting Information for Chapter 6

C.1 ^1H NMR Measurements of SnEHA

Figure C.1 shows the ^1H NMR spectra of as-purchased SnEHA and purified SnEHA. The spectra were recorded using a spectrometer consisting of an Ascend 400 magnet and an Avance III HD 400 console (Bruker) with 8 scans, an acquisition time of 5 s, and a relaxation delay of 30 s. The peak at a chemical shift of approximately 11 ppm corresponds to the OH group of EHA [35, 190] and should therefore not be present in pure SnEHA.

Assuming EHA is the only impurity, the mole fraction of SnEHA, which is used as a measure of the purity here, can be calculated as follows:

$$x_{\text{SnEHA}} = 1 - \frac{\frac{A_2''}{15}}{\frac{A_2'}{30} + \frac{A_2''}{15}} = 1 - \frac{A_1}{\frac{1}{30}(A_2 - 15A_1) + A_1} \quad (\text{C.1})$$

Therein, A_1 is the integrated area of the OH peak at 11 ppm, and A_2 is the total area of the peaks between approximately 0 and 2 ppm, which contains the signals from all 30 hydrogen atoms of SnEHA (subarea A_2') and those from the 15 non-OH hydrogens of EHA (subarea A_2''). The evaluation yielded $x_{\text{SnEHA}} = 0.67 \text{ mol mol}^{-1}$ for the as-purchased SnEHA and $x_{\text{SnEHA}} = 0.98 \text{ mol mol}^{-1}$ for the purified SnEHA.

Purified SnEHA has a higher viscosity than as-purchased SnEHA. This was confirmed in preliminary viscosity measurements (not reported here due to the low purity of as-purchased SnEHA) and also becomes visible in the spectra due to the consequent reduction of the relaxation time increasing the line width and thereby decreasing the level of detail in the spectrum.

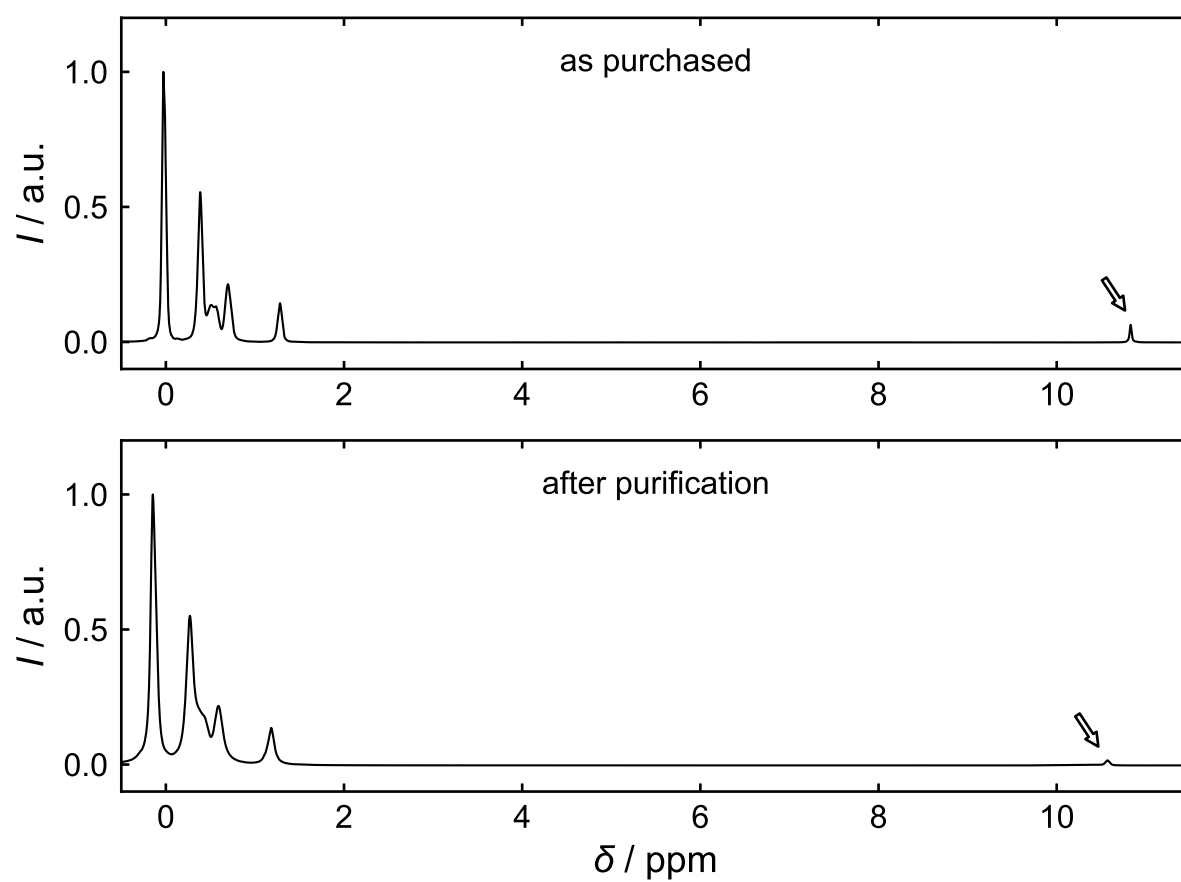


Figure C.1: ^1H NMR spectra of SnEHA as purchased (top) and after purification (bottom). The arrows point to the OH peak of EHA, which should not be present in pure SnEHA.

C.2 Excess Properties and Deviations

Figure C.2 and Figure C.3 show the excess contributions to the molar volume and the isobaric heat capacity, respectively. Figure C.4 shows the deviation of the thermal conductivity from linear behavior with respect to the molar composition, analogously to the modeling approach for the molar volume and the isobaric heat capacity (cf. Eqs. (5) and (7)). The excess or deviation contributions of the molar volume, the isobaric heat capacity, and the thermal conductivity are small, especially in relation to the measurement uncertainty of the experimental results. For the viscosity, the deviation contribution is defined in accordance with the Jouyban-Acree correlation (cf. Eq. (10)):

$$\eta^{\text{dev}} = \eta - (\eta_{\text{SnEHA}}^{\text{pure}})^{x_{\text{SnEHA}}} (\eta_{\text{Xyl}}^{\text{pure}})^{x_{\text{Xyl}}} \quad (\text{C.2})$$

The deviation contribution of the viscosity is shown in Figure C.5.

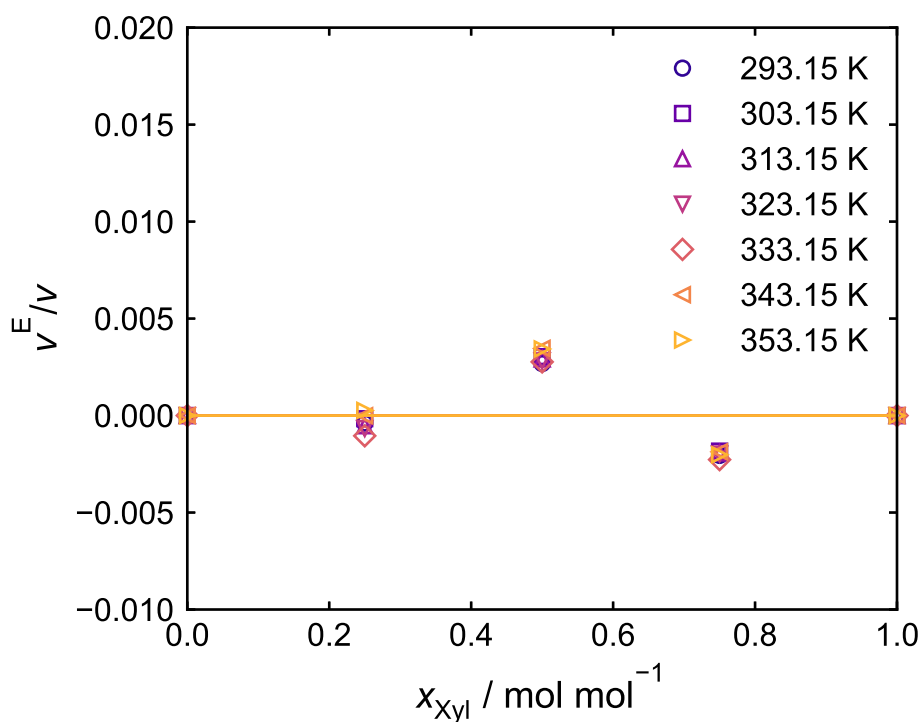


Figure C.2: Relative excess molar volume v^E/v of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Lines are empirical correlations, cf. Eq. (7), with parameters listed in Table 33.

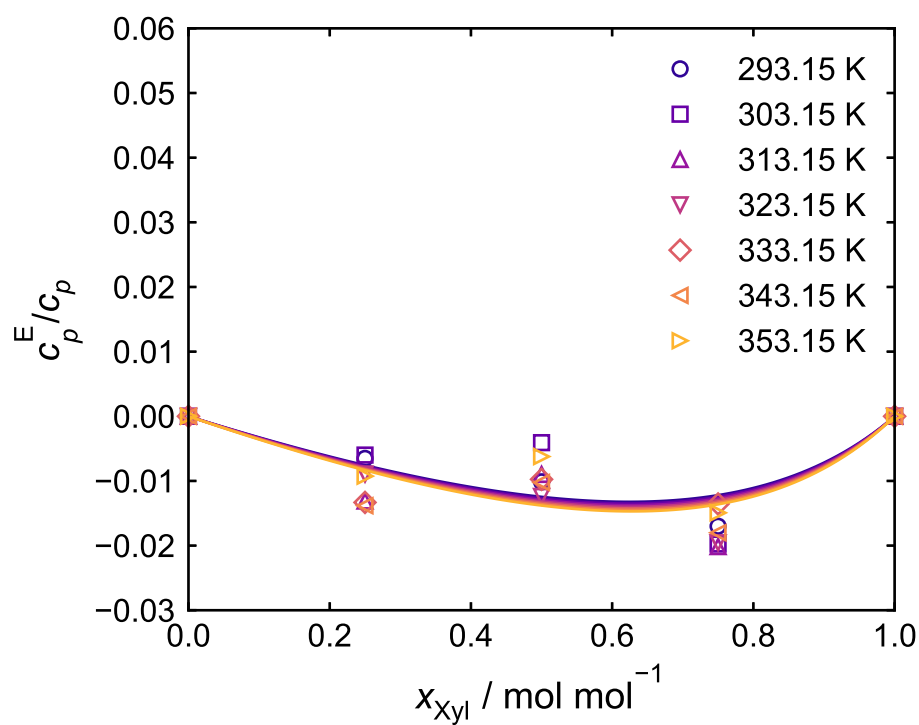


Figure C.3: Relative excess isobaric heat capacity c_p^E/c_p of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Lines are empirical correlations, cf. Eq. (7), with parameters listed in Table 33.

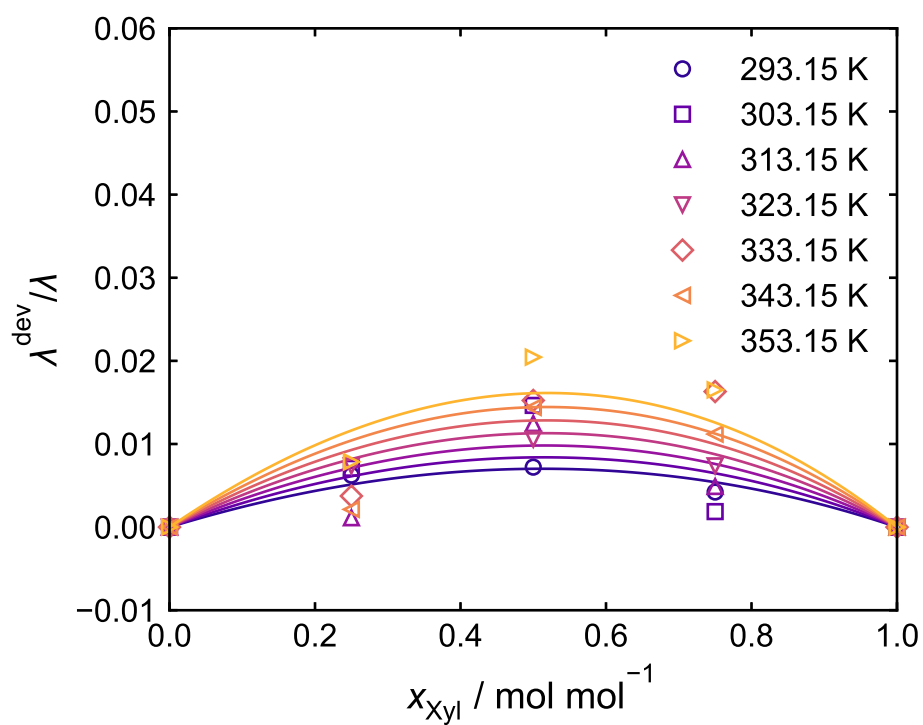


Figure C.4: Relative thermal conductivity deviation $\lambda^{\text{dev}}/\lambda$ of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Lines are empirical correlations, cf. Eq. (7), with parameters listed in Table 33.

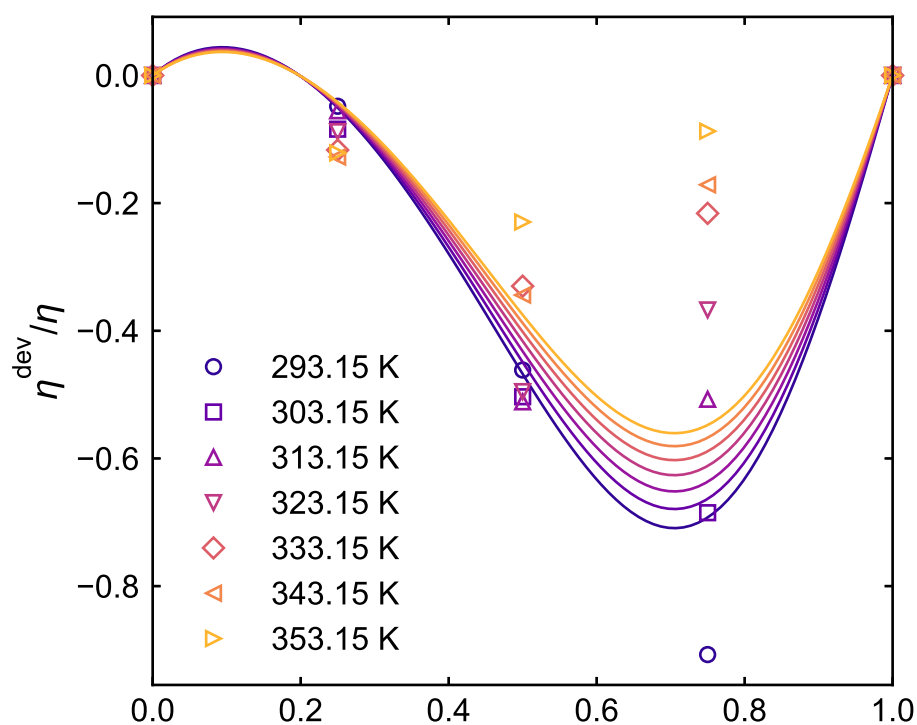


Figure C.5: Relative viscosity deviation η^{dev}/η of mixtures of SnEHA and *p*-xylene at 101.3 kPa and different temperatures. Symbols are experimental results. Lines are empirical correlations, cf. Eq. (10), with parameters listed in Table 33.

D Supporting Information for Chapter 7

D.1 Relevance of the Esterification Reaction of EHA with Ethanol

Before carrying out the LLE measurements, a preliminary investigation was conducted to determine if the esterification reaction (I) between EHA and ethanol to ethyl 2-ethylhexanoate (EEH) and water plays a role in the experiments. Two samples, each weighing 10 g, of an equimolar mixture of EHA and ethanol were prepared. A small amount (0.2 g) of dilute sulfuric acid H_2SO_4 (CAS 7664-93-9, Supelco, specified concentration 1 mol l^{-1}) was added to one of the samples to act as a catalyst.

Both samples were kept in closed screw-top vials at atmospheric pressure and room temperature for three months. Then, the sample composition was analyzed using ^{13}C NMR spectroscopy. The NMR spectrometer was a Bruker Ascend 400 magnet with a magnetic field strength of 9.4 T and a Bruker Avance III HD 400 console. The spectra were recorded with an acquisition time of 3.8 s per scan, 64 scans and a relaxation delay of 60 s. The postprocessing of the NMR spectra was done with MestReNova v12.2.2 by Mestrelab Research S.L.. An automatic phase correction was applied. The peak integration was done manually.

Figure D.1 shows the ^{13}C NMR spectra of the samples without (top) and with (bottom) H_2SO_4 as the catalyst. The spectrum of the mixture without catalyst does not show any distinct peaks corresponding to the ester (EEH), except for a tiny peak at a chemical shift of about 23 ppm. Hence, only a very small amount of the ester forms without a catalyst even after three months. By contrast, for the mixture with catalyst, the peak at a chemical shift of about 23 ppm is clearly visible, and also other peaks of the ester can be discerned from those of EHA.

The compositions of the samples were calculated from the integration of the peaks. Water is not visible in the ^{13}C NMR spectra but because of the stoichiometry of reaction (I),

the molar amount of water formed in the reaction has to be the same as that of the ester. Therefore, the mole fraction of EEH was calculated as follows:

$$x_{\text{EEH}} = \frac{A_{\text{EEH}^{(8)}}}{A_{\text{EHA}^{(8)}} + A_{\text{EtOH}^{(2)}} + 2A_{\text{EEH}^{(8)}}}, \quad (\text{D.1})$$

where $A_{i(j)}$ is the peak area of peak j of component i (see Figure D.1). The ester mole fractions were $x_{\text{EEH}} \approx 0.006 \text{ mol mol}^{-1}$ and $x_{\text{EEH}} \approx 0.155 \text{ mol mol}^{-1}$ in the samples without and with H_2SO_4 , respectively. Hence, it is safe to neglect the esterification reaction in the evaluation of the LLE measurements and the model development presented in Chapter 7.

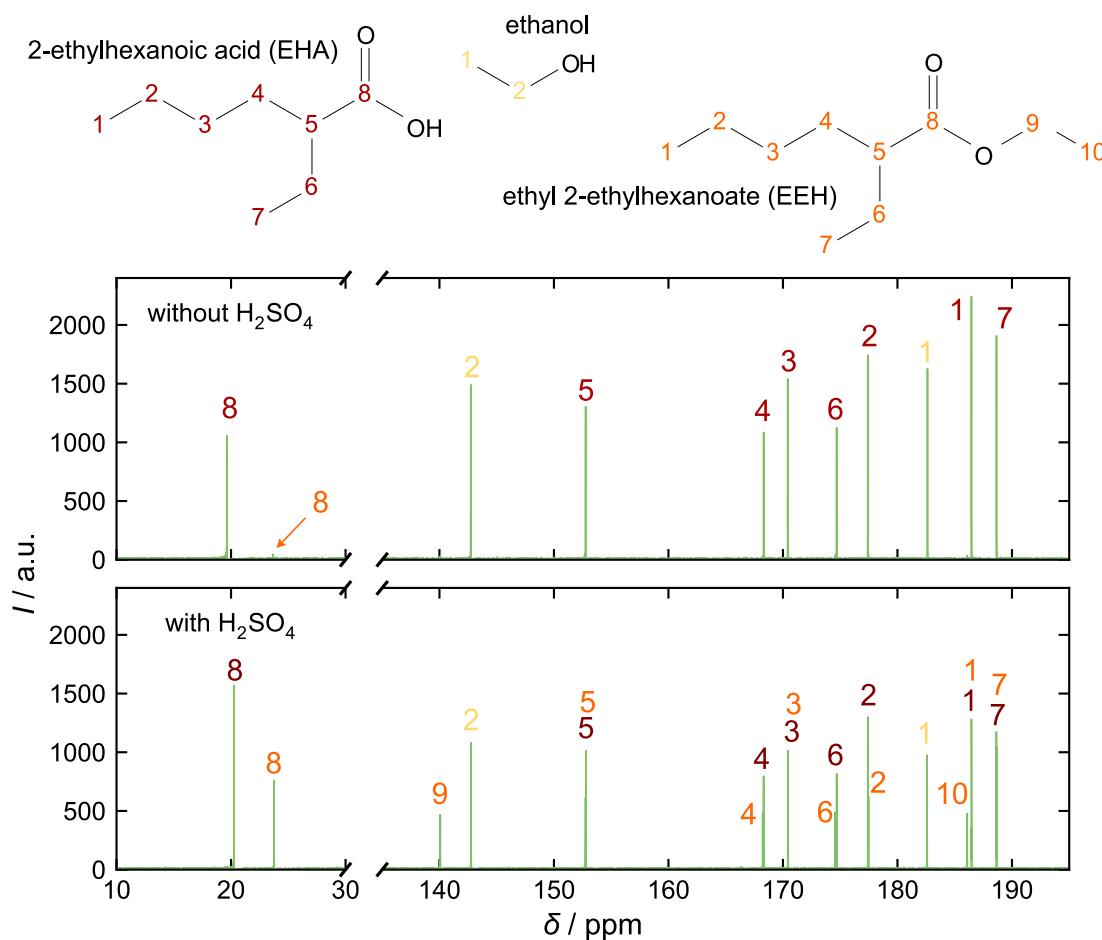


Figure D.1: ^{13}C NMR spectra of mixtures of EHA and ethanol without (top) and with (bottom) addition of H_2SO_4 as a catalyst for the esterification reaction and corresponding peak assignment.

Declaration

This dissertation contains material that has been published previously or that is included in submitted publications. In the following, these publications are listed together with a statement on the contributions of the author of the present dissertation.

- B. Kunstmann, M. Kohns, H. Hasse: Thermophysical Properties of Mixtures of 2-Ethylhexanoic Acid and Ethanol, *Journal of Chemical and Engineering Data*, 68 (2023) 330 – 338, DOI: 10.1021/acs.jced.2c00689.
The author carried out or supervised the experiments. The author evaluated the results and developed the thermodynamic models and correlations. The author wrote the manuscript.
- B. Kunstmann, H. Hasse, M. Kohns: Thermophysical Properties of Mixtures of 2-Ethylhexanoic Acid and *p*-Xylene, *Journal of Chemical and Engineering Data*, 69 (2024) 3383 – 3391, DOI: 10.1021/acs.jced.3c00686.
The author carried out or supervised the experiments. The author evaluated the results and developed the thermodynamic models and correlations. The author wrote the manuscript.
- B. Kunstmann, H. Hasse, M. Kohns: Thermophysical Properties of Mixtures of Tin(II) 2-Ethylhexanoate and *p*-Xylene, *Journal of Chemical and Engineering Data*, 70 (2025) 227 – 235, DOI: 10.1021/acs.jced.4c00459.
The author carried out or supervised the experiments. The author evaluated the results and developed the thermodynamic models and correlations. The author wrote the manuscript.
- B. Kunstmann, H. Hasse, M. Kohns: Liquid-Liquid Equilibria in Mixtures of 2-Ethylhexanoic Acid, Ethanol, and Water, *Journal of Chemical and Engineering Data*, 69 (2024) 3111 – 3117, DOI: 10.1021/acs.jced.4c00345.
The author carried out or supervised the experiments. The author evaluated the results and developed the thermodynamic models and correlations. The author wrote the manuscript.
- B. Kunstmann, I. Wlokas, M. Kohns, H. Hasse: Simulation Study of Superheating in Evaporating Droplets of (TTIP + *p*-Xylene) in Spray Flame Synthesis, *Applications in Energy and Combustion Science*, 15 (2023) 100156,

DOI: 10.1016/j.jaecs.2023.100156.

The author developed the droplet evaporation model together with the co-authors, implemented the model, performed performed the simulations and evaluated the results. The author wrote the manuscript.

Furthermore, the author contributed to the following publication that is relevant for this thesis:

- D. Schaefer, B. Kunstmann, S. Schmitt, H. Hasse, M. Kohns: Explosions of Nanodroplets Studied with Molecular Dynamics Simulations, *Physics of Fluids*, 36 (2024) 37129, DOI: 10.1063/5.0190455.

Student Theses

The following student theses were prepared under the supervision of the author of the present doctoral thesis in the frame of her research:

- F. Bartzack: Experimental Study and Modeling of the Vapor-Liquid Equilibrium of 2-Ethylhexanoic Acid and *p*-Xylene. Project thesis (Bachelor), Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern (2021).
- H. Kasten: Experimental Study of Thermophysical Properties of Mixtures of 2-Ethylhexanoic Acid with *p*-Xylene or Ethanol. Project thesis (Bachelor), Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern (2021).
- H. Kasten: Liquid-Liquid Equilibria in Mixtures of 2-Ethylhexanoic Acid, Ethanol, and Water. Project thesis (Master), Laboratory of Engineering Thermodynamics (LTD), RPTU Kaiserslautern (2023).

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