Viscosity and Surface Tension of Benzene at Saturation Conditions from Surface Light Scattering

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Abstract

In the present study, the liquid viscosity and surface tension of benzene was determined at saturation conditions from surface light scattering (SLS) experiments between (283 and 393) K. Based on the application of the hydrodynamic theory for surface fluctuations at the vapor–liquid phase boundary which was successfully validated by the measurements, a simultaneous determination of liquid viscosity and surface tension with average relative expanded uncertainties ($k=2$) of (1.0 and 0.8)% was achieved. Agreement between the measurement data and reference values available in the literature was found for the viscosity and in general also for the surface tension, where benzene constitutes a recommended reference material of relatively moderate surface tension values. All these findings demonstrate for a repeated time that SLS is a suitable method for the investigation of fluids including reference fluids such as benzene, which enables a sound representation of its surface tension, presumably as a result of a rather random molecular orientation at the surface. Overall, the experimental results from this work could contribute to an improved data situation for benzene, in particular with respect to providing viscosities and surface tensions at true saturation conditions.

Keywords Benzene · Surface light scattering · Surface tension · Viscosity

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1 Introduction

Surface light scattering (SLS) is a well-established technique for the measurement of viscosity and surface or interfacial tension of fluids [1–3]. The method probes the dynamics of thermally excited fluctuations at phase boundaries by the study of the intensity of the scattered light, which allows to perform measurements at macroscopic thermodynamic equilibrium in a contactless manner without the need for any calibration procedure. For an accurate determination of viscosity and surface tension, both of which can be accessed simultaneously in particular in the case of low-viscosity fluids, it is necessary to apply an exact treatment of the hydrodynamic theory for surface fluctuations [4, 5], whose wave numbers probed in the experiment should be sufficiently large [1, 6]. By fulfilling these requirements, no measurable differences between the values obtained by SLS and by accurate conventional methods can be found [2]. In the context of thermophysical property research, SLS has been applied for the measurement of viscosity and surface tension of various types of working fluids in process and energy engineering [2]. Here, refrigerants [7–9], hydrocarbons [10–12], ionic liquids [13–15], and liquid organic hydrogen carriers (LOHCs) [16, 17] can be mentioned as examples. Furthermore, SLS investigations on the reference fluids toluene [1, 6] and diisodecyl phthalate [18] contributed to the development of standards of low viscosity [19] and moderately high viscosity [20].

Benzene is a key aromatic hydrocarbon and an interesting substance from an industrial point of view, but also from a scientific metrological perspective. It serves as a basic feedstock for the production of chemicals with often more complex structures which are processed to, *e.g.*, polymers [21], textiles or resins [22], and detergents [23]. In the field of renewable energy technology, benzene constitutes the core element of LOHCs in which the dehydrogenated compounds contain typically two or three phenyl rings used for the chemical storage and release of hydrogen [24, 25]. Despite its unfavorable features such as toxicity and carcinogenicity, benzene is commonly used as a test or reference substance in measurement equipments [26–31] due to its well characterized properties including high purity. In this connection, benzene is a recommended reference material for surface tension with relatively moderate values of $28.9 \text{ mN}\cdot\text{m}^{-1}$ at 293.15 K [31] and is, thus, often employed to check or calibrate tensiometers [26, 27, 31, 32].

Investigations on the viscosity and surface tension of benzene by SLS, which are lacking until now, are stimulated by various reasons. From our currently ongoing studies on LOHC systems based on diphenylmethane (DPM) [16, 17], it was found that the surface tensions obtained from SLS are between about (6 to 1)% smaller than data from the conventional pendant drop method for temperatures from (303 to 523) K [16]. Such discrepancies, which are comparable or even larger for mixtures of DPM with its hydrogenated counterpart and for the partially hydrogenated intermediate cyclohexylphenylmethane [17], indicate possible molecular orientation effects at the fluid interface causing a self-induced surface dipole moment or charge polarization [33, 34]. These effects seem to alter the dynamics of the surface fluctuations in fluids with a preferred interfacial

orientation, that is more pronounced at lower temperatures or larger viscosities, respectively, in a way that the application of the classical hydrodynamic theory [4, 5] which does not account for these effects results in underestimated apparent surface tensions [34], while the viscosity as bulk property is evidently not affected. In this context, the selection of benzene for the present SLS study is reasonable as it forms the building block of the above LOHCs, features a distinctly lower viscosity than the latter, and serves as a reference fluid for surface tension. All these characteristics allow to probe whether discrepancies in the surface tension are also visible for the bare aromatic ring. Here, recent experiments by sum-frequency generation evidenced a random surface orientation of benzene without preferential alignment [35], which would lead to the expectation, yet unproven, that no falsifying impact on the surface tension of benzene evaluated from SLS experiments should be present.

Although a relatively large experimental database exists for the surface tension of benzene, as has been summarized by Mulero et al. [36] and Součková et al. [26], it appears that most surface tension measurements were performed in the presence of an air atmosphere and, thus, not at true saturation conditions. The value of the surface tension is very sensitive to impurities and contaminations which can originate from the sample itself or can be introduced by the gas atmosphere such as air being in direct contact with the substance of investigation. Overall, the necessity to realize surface tension measurements at or very close to equilibrium is often in conflict with the working principle of conventional tensiometry. In this context, SLS investigations are of particular advantage since the measurements are carried out in macroscopic thermodynamic equilibrium at true saturation conditions [2]. The latter conditions are usually also not given for the measurement results for the liquid viscosity of benzene. Here, the primary data sets considered in the reference correlation of Avgeri et al. [37] are associated with the presence of ambient air or a compressed liquid state.

The main objective of the present study is the accurate determination of the liquid viscosity and surface tension of benzene at saturation conditions in the temperature range between (283 and 393) K. This should not only allow to contribute to an extended database for both thermophysical properties, but also to elucidate whether the SLS method gives reliable access to the surface tension of the reference fluid benzene, as it is anticipated from its random surface orientation. In the following, a brief introduction to the SLS technique and its experimental procedure is given, followed by a measurement example and the data evaluation, with a special focus on the check of the hydrodynamic theory which could be validated by experiments. Thereafter, the results for viscosity and surface tension are presented and discussed by comparison with available literature data.

2 Surface Light Scattering (SLS)

2.1 Theoretical Background

The fundamentals of SLS for the accurate determination of liquid dynamic viscosity η' and surface tension σ by the analysis of capillary waves at the phase boundary

between a liquid and a vapor phase are only summarized briefly in the following. A detailed description of the underlying theory and methodological principles can be found elsewhere [1–4].

Light scattered at the interface is modulated by the surface fluctuations with a defined modulus of the wave vector q and, thus, contains information about their dynamics. By means of photon correlation spectroscopy, the temporal behavior of the scattered light intensity reflected by the dynamics of the surface fluctuations is analyzed in time-dependent correlation functions (CFs). For benzene in the studied range of temperatures and wave vectors, the surface fluctuations having wavelengths in the μm range and amplitudes on the order of nm integrated over all wavelengths were propagative associated with an oscillatory behavior. Thus, all normalized intensity CFs recorded within this study in a heterodyne detection scheme can be described by a damped oscillation [4]

$$g^{(2)}(\tau) = a + b \cos(\omega_q |\tau| - \phi) \exp(-|\tau|/\tau_C). \quad (1)$$

The parameters a and b represent experimental constants governed by the coherence properties of the system and the ratio of light scattered at the interface to the superimposed reference light. The phase term ϕ mainly reflects the deviation of the spectrum from the Lorentzian shape. τ_C and ω_q describe the mean lifetime or the inverse of the damping ($\tau_C = \Gamma^{-1}$) of the probed fluctuations and their frequency of propagation, respectively.

For the accurate simultaneous determination of η' and σ at saturation conditions, the dispersion relation $D(\eta', \eta'', \rho', \rho'', \sigma, \Gamma, \omega_q, q)$ for surface fluctuations at the phase boundary between a liquid ('') and a vapor (') phase [4, 5] was considered in its complete form. In addition to the information on the dynamics of the surface fluctuations, *i.e.*, Γ and ω_q , obtained from the SLS experiment, reference data for the density of the liquid phase ρ' and vapor phase ρ'' as well as for the dynamic viscosity of the vapor phase η'' under saturation conditions were utilized.

2.2 Experimental Section

Benzene (CAS no. 71-43-2) was purchased from Merck KGaA in high performance liquid chromatography (HPLC) grade with a specified mass purity of 99.9 % and used without further treatment. The used optical and electronic arrangement of the SLS setup analyzing the scattered light in transmission direction perpendicular to the phase boundary is identical to the one employed in Ref. [16] and is described in detail in Refs. [1, 2]. A sample cell made of aluminum was employed in this study, which has already been used for the investigation of, *e.g.*, toluene [1, 6].

Before filling, the sample cell was successfully checked regarding tightness up to 1 MPa and down to 10^{-6} MPa, which covers well the range of saturation pressures of benzene between (6×10^{-3} and 0.3) MPa corresponding to the investigated temperatures between (283.15 and 393.15) K [38]. Benzene was then filled from a reservoir through a thin capillary into the evacuated sample cell to ensure true saturation conditions. The regulation of the temperature of the sample cell inside an insulated

housing was realized by resistance heating. For measurements below ambient temperature, the housing around the sample cell was cooled about 10 K below the measurement temperature T . The latter was recorded inside the main body of the sample cell by two calibrated Pt-100 resistance probes with an expanded uncertainty (coverage factor $k=2$) of 15 mK, one of which was used for temperature control. The readings of both probes agreed always within combined uncertainties and typically within the single uncertainty, which allowed to consider the recorded temperature of the control sensor as temperature state T reported in this study. The temperature stability defined by the standard deviation of the recorded temperatures throughout an experimental run was better than ± 2 mK for all investigations.

For each investigated T state, six measurements have been performed at different wave vectors $q=2\pi/\lambda_0 \cdot \sin(\Theta_E)$ corresponding to different external angles of incidence Θ_E between $(3.0 \text{ and } 3.9)^\circ$. Here, complementary angles on either side of the normal with respect to the fluid surface were aligned to avoid errors due to misadjustment. The power of the incident light (wavelength in vacuum $\lambda_0=532 \text{ nm}$) irradiating the benzene surface was always below 65 mW. For data representation, the results for η' and σ obtained from different measurements were averaged. The expanded uncertainties ($k=2$) of the resulting properties were calculated from error propagation schemes [1, 12], considering the precision of the individual measurements and the uncertainties of the relevant input quantities. After experiments at the largest T of 393.15 K, repetition measurements were carried out at (343.15 and 303.15) K. The corresponding results were found to agree within their uncertainties with the first measurement, which confirms the stability of the benzene sample and the reproducibility of the results. Thus, the average from both measurement sets at (303.15 and 343.15) K is stated together with the smaller of the two respective uncertainties. The same procedure was also applied to the two measurement sets at 298.15 K performed at the end of the investigations on benzene.

2.3 Measurement Example and Data Evaluation

Figure 1 shows an example of a normalized intensity CF obtained from an SLS experiment at the benzene surface at 303.15 K and an external angle of incidence of 3.1° . As for all recorded heterodyne CFs, the signal was fitted based on Eq. 1 using the Levenberg–Marquardt algorithm, resulting in values and expanded uncertainties ($k=2$) of $\tau_C=(2.424 \pm 0.024) \mu\text{s}$ and $\omega_q=(2.735 \pm 0.004) \times 10^6 \text{ rad}\cdot\text{s}^{-1}$ for the illustrated measurement example. The fit residuals given in the lower part of Fig. 1 are free of systematics, which confirms that the fit accurately describes the recorded signal. Considering all CFs recorded within this work, the relative uncertainties for the frequency ω_q and damping Γ are on average $U_r(\omega_q)=0.15 \%$ and $U_r(\Gamma)=1.1 \%$.

To perform an exact numerical solution of the dispersion relation for surface fluctuations [4, 5], the experimentally acquired quantities ω_q and Γ for defined q values were combined with reference data for ρ' , ρ'' , and η'' . For ρ' and ρ'' , calculated values from the REFPROP database [38] on the basis of the work of Thol et al. [39] with relative expanded uncertainties of $U_r(\rho')=(0.1 \text{ or } 0.2)\%$ for T below or above 350 K, respectively, and $U_r(\rho'')=1 \%$ were employed. For η'' with uncertainties

Fig. 1 Measurement example of a normalized intensity CF recorded by SLS (upper part) and the fit residuals (lower part) for benzene at saturation conditions at 303.15 K using an external angle of incidence of 3.1° as a function of the lag time τ : $\square$, measurement data; —, fit according to Eq. 1

$U_r(\eta'')=0.2\%$, the data were employed from the reference correlation of Avgeri et al. [37], which is also recommended by REFPROP [38]. The contributions of the uncertainties of the individual input parameters to the uncertainties of η' and σ has been studied in detail for different fluids with properties similar to benzene in Refs. [1, 12]. Also in the case of benzene, the contribution of $U_r(\rho'')$ and $U_r(\eta'')$ to the overall uncertainties are negligibly small compared to that of $U_r(\rho')$ and the uncertainty given by the double standard deviation of the results from six independent measurements at a given T .

For probing the validity of the hydrodynamic theory [4, 5], the dynamics of the surface fluctuations of saturated benzene was studied over a wide range of incident angles between $(2.5 \text{ and } 6.5)^\circ$, corresponding to a broad range of wave vectors between $(0.52 \text{ and } 1.3) \times 10^6 \text{ m}^{-1}$. Figure 2 shows the experimental results for the damping Γ ($=1/\tau_c$) and frequency ω_q at 303.15 K as function of q in comparison with the values predicted by the exact form of the dispersion relation [4, 5]. For its evaluation, besides the application of the aforementioned reference data for ρ' , ρ'' , and η'' , the values for the liquid viscosity η' and the surface tension σ are based on the reference correlations published by Avgeri et al. [37] and Mulero et al. [36], respectively, both of which are also recommended in the REFPROP database [38].

As can be seen from the upper part of Fig. 2, the experimental results for the damping Γ agree with the theoretical ones over the entire range of investigated wave vectors. For the frequency ω_q shown in the lower part of Fig. 2, the measurement results are about 1 % lower than the ones calculated based on literature data for all wave vectors studied. This is reflected in corresponding deviations of our experimental results for σ from the correlation of Mulero et al. [36], as it will be discussed later on. Since the weak discrepancy in ω_q remains constant with varying q , the hydrodynamic theory for surface fluctuations [4, 5] is also validated for the measured frequencies, meaning

Fig. 2 Damping (upper part) and frequency (lower part) of surface fluctuations of benzene at saturation conditions at 303.15 K as a function of the wave vector q : $\square$, measurement; —, hydrodynamic theory [4, 5] based on input quantities described in the text

that no anomalous effects induced by molecular surface orientation seem to be present for benzene. These effects would give rise to a different behavior of the frequencies in dependence on the wave vector than expected from the classical hydrodynamic theory [33, 34], which has not been observed here.

To exclude influences from instrumental line broadening which become more dominant with decreasing q [1, 4], only wave numbers larger than $0.6 \times 10^6 \text{ m}^{-1}$ were considered for the evaluation of η' and σ . Using a full theoretical description of the dynamics of surface fluctuations [4, 5], the liquid viscosity and surface tension of saturated benzene could be determined simultaneously with total expanded ($k=2$) relative uncertainties between $U_r(\eta')=(0.47 \text{ and } 1.4) \%$ and $U_r(\sigma)=(0.44 \text{ and } 1.2) \%$.

3 Results and Discussion

The results for the liquid dynamic viscosity η' and surface tension σ of benzene from SLS experiments at saturation conditions for temperatures T between (283.15 and 393.15) K together with their uncertainties are summarized in Table 1. Therein, also the calculated values for ρ' , ρ'' , and η'' reported in the REFPROP database [38] and

Table 1 Liquid viscosity η' and surface tension σ of benzene at saturation conditions as a function of temperature T obtained by SLS together with literature data for liquid density ρ' , vapor density ρ'' , and vapor viscosity η''

T (K)	ρ' (kg·m ⁻³)	ρ'' (kg·m ⁻³)	η'' (μPa·s)	η' (mPa·s)	$100 \cdot U_r(\eta')$	σ (mN·m ⁻¹)	$100 \cdot U_r(\sigma)$
283.15	889.3	0.203	7.19	0.7592	1.0	29.39	1.2
293.15	878.8	0.323	7.44	0.6498	0.61	28.20	1.0
298.15	873.6	0.403	7.56	0.6033	0.63	27.44	0.66
303.15	868.3	0.497	7.68	0.5644	1.0	26.89	0.86
313.15	857.7	0.740	7.92	0.4981	0.93	25.60	0.68
323.15	847.0	1.07	8.16	0.4429	0.84	24.36	0.97
333.15	836.1	1.51	8.39	0.3952	0.47	23.04	0.55
343.15	825.1	2.07	8.63	0.3520	0.84	21.84	0.68
353.15	814.0	2.78	8.86	0.3212	1.2	20.67	0.67
363.15	802.6	3.68	9.10	0.2906	0.96	19.54	0.90
373.15	791.1	4.78	9.33	0.2666	1.3	18.24	1.2
383.15	779.3	6.12	9.56	0.2437	1.4	17.05	0.44
393.15	767.3	7.74	9.79	0.2245	1.4	15.88	1.1

Directly measured values for damping Γ and frequency ω_q at a defined wave vector q of surface fluctuations were combined with data for ρ' , ρ'' , and η'' obtained from the REFPROP database [38] to determine η' and σ by an exact numerical solution of the dispersion relation [4, 5]. The expanded ($k=2$) uncertainty for the temperature is $U(T)=0.015$ K. The expanded ($k=2$) relative uncertainties for the employed properties are $U_r(\rho')=(0.1$ or $0.2)\%$, $U_r(\rho'')=1\%$, and $U_r(\eta'')=0.2\%$. For the liquid dynamic viscosity and interfacial tension, the relative expanded ($k=2$) uncertainties $U_r(\eta')$ and $U_r(\sigma)$ are given in the table

used as input for data evaluation are listed. The average expanded ($k=2$) uncertainty of the experimental data are 0.97 % for η' and 0.84 % for σ .

3.1 Liquid Viscosity

Within the investigated temperature range, the experimental SLS data for the dynamic liquid viscosity η' can be described by a simple Andrade equation [40] according to

$$\eta'_{\text{calc}} = \eta_0 \exp\left(\frac{\eta_1}{T}\right). \quad (2)$$

By unweighted fitting of Eq. 2 to the experimental data, the fit parameters $\eta_0=9.9789 \cdot 10^{-3}$ mPa·s and $\eta_1=1224.6$ K were obtained. All experimental data are represented by the equation within their experimental uncertainties and show a root mean square (rms) deviation of 0.37 % relative to Eq. 2.

In Fig. 3, the results for the liquid viscosity of benzene obtained at saturation conditions by SLS are shown as a function of temperature in comparison with relevant literature data. While the upper part of Fig. 3 displays the absolute viscosity data, the relative deviations of the present and literature data from the correlation according

Fig. 3 Liquid dynamic viscosity of benzene at saturation conditions from SLS including the fit correlation (—, Eq. 2) as a function of temperature in comparison with literature data detailed in the text: ●, this work; -----, reference correlation from Avgeri et al. [37]; △, Bauer and Meerlender [28]; ▲, Matsuo and Makita [41]; □, Mamedov et al. [42]; ■, Dymond et al. [43]; ◇, Kashiwagi and Makita [44]; ◆, Vieira dos Santos and Nieto de Castro [29]; ✕, Parkhurst and Jonas [45]; ○, Knapstad et al. [46]; ×, Assael et al. [47]. Error bars representing the expanded ($k=2$) uncertainty are shown exemplarily for the present SLS data

to Eq. 2 are given in the lower part of Fig. 3, covering a temperature range from (280 to 400) K. In connection with the literature data, the reference correlation from the triple point at 278.67 K to 675 K and pressures up to 300 MPa developed by Avgeri et al. [37] was applied at saturation conditions, for which η' is associated with an uncertainty of 1.8 % up to 373 K and 2.7 % above. In addition, the corresponding primary experimental data sets, which were used as input for the correlation of Avgeri et al. [37], are shown in Fig. 3. Here, only the respective measurements performed either at atmospheric pressure in the presence of air or at 0.1 MPa in the compressed liquid state are considered, resulting in 33 experimental data points in total. Since a change in pressure of 0.1 MPa will not change the viscosity of benzene by more than 0.09 % in the relevant temperature range [38], differences between the viscosity at the saturation line and at 0.1 MPa are insignificant and, thus, permit the following data comparison.

The primary data are based on capillary measurements performed by Bauer and Meerlender [28] as well as Matsuo and Makita [41] with stated uncertainties of 0.7 % and 2 %, respectively, falling body measurements from Mamedov et al. [42] and Dymond et al. [43] with uncertainties of 1 % and 2 %, respectively, and experiments obtained by the torsional crystal method from Kashiwagi and Makita [44] as well as from Vieira dos Santos and Nieto de Castro [29] with uncertainties of 2 % and 0.5 %, respectively. Furthermore, the viscosity results from Parkhurst and Jonas [45], Knapstad et al. [46], and Assael et al. [47] who applied the rolling ball, oscillating cup, and vibrating wire techniques with estimated uncertainties of about 2.5 %, 1.0 %, and 0.5 %, respectively, are included in the primary database. For converting the

kinematic viscosities ν reported by Bauer and Meerlender [28] to dynamic viscosities η , density data from the REFPROP database [38] were utilized.

As can be seen from the deviation plot in Fig. 3, excellent agreement between the viscosity data from literature with the ones presented in this work is found over the whole T range. With the exception of the single data point at 348 K reported by Vieira dos Santos and Nieto de Castro [29], which deviates by -5.3% from Eq. 2 and is not shown in the lower part of Fig. 3, the literature values agree with our correlation based on Eq. 2 within combined uncertainties. This is also reflected by the behavior of the reference correlation of Avgeri et al. [37] which shows a maximum deviation of 0.78% from our experimental results between (283 and 393) K. Overall, the present viscosity data obtained from SLS and, in contrast to the aforementioned experimental literature data, associated with saturation conditions represent the viscosity behavior well at temperatures close to the triple point of benzene and could extend the database at temperatures above 350 K. These current findings for benzene are in accordance with those observed for many other fluid types [2, 11, 12, 48] including the reference fluids toluene [1, 6] and diisodecyl phthalate [18], which demonstrates that SLS gives accurate and reliable access to the true shear viscosity of the bulk of the fluid.

3.2 Surface Tension

The experimental data for the surface tension of benzene obtained from SLS can be described by a linear temperature-dependent fit of the form

$$\sigma = \sigma_0 + \sigma_1 T. \quad (3)$$

In Eq. 3, the parameters determined from an unweighted fit procedure are $\sigma_0 = 64.135 \text{ mN}\cdot\text{m}^{-1}$ and $\sigma_1 = -0.12296 \text{ mN}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Except for the value at 333.15 K, the fit represents the experimental data points within their stated uncertainties, resulting in a rms deviation of 0.32% relative to Eq. 3.

Figure 4 compares the surface tension of benzene obtained at saturation conditions by SLS with accessible literature data published within the last about one hundred years in form of an absolute and relative plot in the upper and lower part, respectively. For the data comparison in the T range between (280 and 400) K, only literature sources were considered where at least four experimental σ values at different temperatures within a temperature range of at least 10 K are reported. For most of the in total 73 experimental data displayed in Fig. 4 and differentiated in the following, measurements were performed at a pressure of about 0.1 MPa in the presence of a contacting air atmosphere, which is presumably also given in the corresponding studies where no details on the pressure or the surrounding atmosphere are specified.

In detail, the drop weight technique was employed by Harkins et al. [49], Morgan and Scarlett [50], and Harkins and Cheng [51] with uncertainties for the surface tension of approximately 1% , 2.5% , and 2.5% , respectively, whereby in all cases no information about the surrounding conditions can be found. The latter statement

Fig. 4 Surface tension of benzene at saturation conditions from SLS including the fit correlation (—, Eq. 3) as a function of temperature in comparison with literature data detailed in the text: ●, this work; ----, correlation from Mulero et al. [36]; □, Harkins et al. [49]; ■, Morgan and Scarlett [50]; ▤, Harkins and Cheng [51]; ▽, Jäger [52]; △, Bowden [53]; ▲, Muratov [54]; ▽, Sugden [27]; ◇, Schmidt et al. [32]; ◆, Prabhakar et al. [55]; ○, Bonnet and Pike [56]; ●, Součková et al. [26]; ×, Lopez-Lazaro et al. [57]. Error bars representing the expanded ($k=2$) uncertainty are shown exemplarily for the present SLS data

holds also for the measurements of Jäger [52], Bowden [53], and Muratov [54] who applied the capillary rise method with uncertainties of about 2.5 %, (1 to 3)%, and 2.5 %, respectively. Without providing uncertainty statements, the maximum bubble pressure method was applied in the presence of an air atmosphere by Sugden [27] and at saturation conditions by Schmidt et al. [32]. The same method was utilized by Prabhakar et al. [55] who specified an uncertainty of 0.35 % for the surface tension related to the interface between liquid benzene and air. Such an experimental situation was also given in the measurements from Bonnet and Pike [56] and Součková et al. [26] using the Wilhelmy plate technique with uncertainties of about 1.5 % in each case as well as those from Lopez-Lazaro et al. [57] employing the drop volume method with associated uncertainties of approximately 0.1 %. It is expected that most of the above experimental data sets are also included in the correlation developed by Mulero et al. [36] who regarded a larger yet undifferentiated database for benzene than it is given here. Since the correlation of Mulero et al. [36] showing an average absolute deviation of 1.32 % for the surface tension of benzene from the 233 considered datapoints is also recommended by REFPROP [38], it has been incorporated in Fig. 4.

According to the deviation plot in Fig. 4, where the relative percentage deviations of the present SLS results and of the literature values from the correlation based on Eq. (3) are depicted, the maximum differences between the different data sets are about 5 %. Most of the experimental data as well as the correlation of Mulero et al. [36] are

between about (2 and 4)% larger than our experimental data, whereby the deviations tend to decrease with increasing temperature. Compared to the value for the surface tension of the benzene-air interface at 293.15 K with $(28.88 \pm 0.01) \text{ mN}\cdot\text{m}^{-1}$ recommended by IUPAC in the year 1987 [31], our experimental value for saturated benzene with $(28.20 \pm 0.28) \text{ mN}\cdot\text{m}^{-1}$ is -2.4% lower, which is outside combined uncertainties. The same behavior can be observed when accounting for the standard reference data for the vapor-liquid surface tension of benzene provided by Součková et al. [26], which are basically identical to the values from the correlation of Mulero et al. [36] and are not shown in Fig. 4. Considering the data set of Muratov et al. [54] covering the broadest T range among the literature values between (293 and 393) K and the recommended correlation [36] with an estimated uncertainty of 2 %, the deviations from the SLS data are within combined uncertainties. Such agreement can also be found in connection with the measurement results from Jäger [52] and Morgan [50].

Differences in the published data for the surface tension of benzene, which could also be seen in a similar way for, *e.g.*, toluene [1, 6] and linear alkanes [11, 12], seem to be affected by experimental conditions and specifications, which hinders a clear judgment about the quality of the measurements. Uncertainties of experimental surface tensions are in most cases either relatively small below 0.5 % [55, 57] or not specified [27, 32]. Furthermore, besides the potential impact of impurities which can rather be neglected for benzene, contaminations from the air atmosphere being often in direct contact with the fluid of interest may be introduced. As a further consequence, the temperature at the surface of the fluid may be lower than the recorded temperature associated with the surface tensions which are in turn overestimated. Such effects are excluded for the present SLS investigations as they are carried out in macroscopic thermodynamic equilibrium at saturation conditions.

In consideration of the representation of the hydrodynamic theory by the measured data for damping and frequency, as it was shown in connection with Fig. 2, and the sound agreement of the present surface tensions with literature, it is believed that the surface tension results for benzene obtained from SLS can be regarded as trustable values for this reference fluid. This allows to derive the conclusion that for fluids with negligible surface orientation effects, as it is given for benzene [35], accurate surface tension results can be determined from the classical hydrodynamic theory, which has also been the case for various other fluids in previous studies; see, *e.g.* in Refs. [2, 8, 10–12]. On the basis of the findings from the present work, further investigations are currently ongoing, with the aim of establishing relationships between the characteristics of molecules in form of their orientation at the interface and the evaluation of SLS experiments. In this regard, apparent limitations of the classical hydrodynamic theory observed for benzene-based LOHCs [16, 17] seem to have only an impact on the surface tension, but not on the viscosity as bulk property.

4 Conclusions

For the first time, experimental data for the liquid dynamic viscosity and surface tension of benzene from SLS have been presented. Measurements were performed under true saturation conditions over a temperature range from (283 to 393) K

and were evaluated on the basis of an exact treatment of the hydrodynamic theory for surface fluctuations, whose validity was checked successfully. Liquid viscosity and surface tension could be determined simultaneously with average relative expanded uncertainties ($k=2$) of 1.0 and 0.8 %. For the viscosity, very good agreement between the data from SLS and the primary reference data in literature was found, confirming the capability of SLS in an accurate determination of viscosity once more. For the surface tension, larger relative differences between the different literature sources of up to 5 % are present, where the SLS results are in the lower band, but still agree satisfactorily with recommended reference values. Thus, by the selection of benzene as reference material for surface tension, the SLS technique could also be checked regarding its accurate access to the surface tension. This finding also confirmed our expectation that no adulterating influence on the surface tensions of benzene evaluated from SLS should be present, supposedly due to the random molecular orientation of benzene at the fluid surface. The current observations are helpful in future investigations which intend to find interpretations for the discrepancies in surface tensions obtained from SLS on the basis of the classical hydrodynamic theory and those from conventional tensiometry, as they were observed for comparable benzene-based LOHC systems of somewhat bulkier structure than benzene.

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Availability of data and material Experimental data including their uncertainties given in the document.

Declarations

Conflicts of interest All authors declare that they have no conflict of interest.

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