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Thermophysical Properties of a Quaternary Refrigerant Mixture: Comparison of Dynamic Light Scattering Measurements with a Simple Prediction Method

Andreas Paul Fröba · Cristina Botero · Heiko Kremer · Alfred Leipertz

Abstract Dynamic light scattering (DLS) has been used for the measurement of several thermophysical properties of a quaternary refrigerant mixture R-125/143a/32/134a in its liquid phase under saturation conditions. The thermal diffusivity and sound speed have been obtained by light scattering from bulk fluids over a temperature range from about 293 K up to the liquid–vapor critical point. By applying the method of DLS to a liquid–vapor interface, also called surface light scattering (SLS), the saturated liquid kinematic viscosity and surface tension can be determined simultaneously. These properties have been measured from about 243 to 343 K. The results are discussed in comparison with literature data and with a simple prediction method based on the mass-weighted properties of the pure components, expressed as functions of the reduced temperature. Once again, the simple prediction method was shown to be applicable for the calculation of different transport and other thermophysical properties of multicomponent refrigerant mixtures and this with sufficiently high accuracy for technical practice. Moreover, the input data for the simple prediction scheme can be reduced without loss of accuracy by treating binary or ternary mixtures as a subset of the multicomponent mixture.

Keywords Dynamic light scattering · Kinematic viscosity · Prediction · Quaternary mixture · Refrigerants · Sound speed · Surface tension · Thermal diffusivity

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A. P. Fröba (✉) · C. Botero · A. Leipertz
Lehrstuhl für Technische Thermodynamik (LTT),
Friedrich-Alexander-Universität Erlangen-Nürnberg,
Am Weichselgarten 8, 91058 Erlangen, Germany
e-mail: apf@ltt.uni-erlangen.de

A. P. Fröba · H. Kremer · A. Leipertz
ESYTEC Energie- und Systemtechnik GmbH,
Am Weichselgarten 6, 91058 Erlangen, Germany

1 Introduction

Over the past 5 years we have reported the determination of thermal diffusivity, sound speed, viscosity, and surface tension of the refrigerant mixtures R507 (50 mass% R125/50 mass% R143a), R404A (44 mass% R125/52 mass% R143a/4 mass% R134a), R410A (50 mass% R125/50 mass% R32), and R407C (25 mass% R125/23 mass% R32/52 mass% R134a) using dynamic light scattering (DLS) [1,2]. We also focused our investigations on binary mixtures of R125 and R143a with different compositions [3]. In addition to a test of the applicability of the DLS-technique to binary and ternary mixtures and an improvement of the data situation for refrigerant mixtures of technical importance, our interest was directed to the comparison of experimental results with simple prediction methods. These results have suggested that the mixture data can be best predicted by the mass-weighted sum of the pure-component data, expressed as functions of the reduced temperature. The properties of the mixture, Y_{M}, under saturation conditions have thus been predicted according to

$$Y_{\mathrm{M}}(T_{\mathrm{R}}) = \sum_{j} w_j Y_j(T_{\mathrm{R}}), \tag{1}$$

where w_j and Y_j are the mass fraction and the property of component j, respectively, at the reduced temperature $T_{\mathrm{R}} = T/T_{\mathrm{C}}$, with T being the absolute temperature and T_{C} the critical temperature. In contrast to other prediction schemes, the proposed equation allows the calculation of thermophysical properties without adjustable parameters up to the critical point, even if the critical temperature of one of the pure components is exceeded.

The motivation for further experimental investigations by DLS, this time of a quaternary refrigerant mixture of about 20 mass% R125, 30 mass% R143a, 25 mass% R32, and 25 mass% R134a, was based on the question whether this simple approach can also be used for the prediction of multicomponent mixtures with different types of components. Furthermore, it should be shown if a simplification of the prediction procedure is possible by introducing the concept that binary or ternary mixtures can also be treated as the components of a multicomponent mixture. For this, the quaternary mixture composition was fixed, with a mass ratio of R125 to R143a of 2 to 3, because a binary mixture with a corresponding composition of 40 mass% R125 and 60 mass% R143a had already been studied by DLS [3].

In the present paper, some characteristics of the DLS-technique are briefly reviewed and the experimental conditions for the investigations of the quaternary refrigerant mixture are specified. Then the experimental results for the thermal diffusivity, sound speed, kinematic viscosity, and surface tension are presented and discussed in detail in comparison with the simple prediction scheme and literature data.

2 Methods

The main advantage of the DLS-technique relies on the possibility of determining thermophysical properties in macroscopic thermodynamic equilibrium. The method allows an absolute determination of a wide range of thermophysical properties with high accuracy, using basically an identical experimental setup. In the following, only some general aspects of the underlying theory of DLS from bulk fluids and the application of this method to fluid surfaces are described. For a detailed and comprehensive description of the fundamentals and methodological principles of DLS, the reader is referred to the specialized literature [4–6]. A more practical treatment of the method in connection with the determination of thermal diffusivity, sound speed, kinematic viscosity, and surface tension of refrigerants can be found in [7–9].

2.1 Light Scattering from Bulk Fluids

When a fluid sample in macroscopic thermodynamic equilibrium is irradiated by coherent laser light, light scattered from the sample can be observed in all directions. The underlying scattering process is governed by microscopic fluctuations of temperature (or entropy), of pressure, and of species concentration in mixtures. The relaxations of these statistical fluctuations follow the same rules that are valid for the relaxation of macroscopic systems. The decay of temperature fluctuations is governed by the thermal diffusivity a. Pressure fluctuations in fluids are moving with the sound speed u_S and their decay is governed by the sound attenuation D_S. In a fluid mixture, the decay of concentration fluctuations is related to mass diffusivities by a more or less complex way, depending on the number of single species. This is represented in the simplest case of a binary fluid mixture by the binary diffusion coefficient D_{12}. In light scattering experiments, the above-mentioned equalization processes result in a temporal modulation of the scattered light intensity. Information about these processes and hence the thermophysical properties can be derived through a temporal analysis of the scattered light intensity, using photon correlation spectroscopy (PCS).

Whether it is possible to determine signals from concentration fluctuations is mainly governed by the relative difference of the refraction indices of the mixture components and their concentration. For the quaternary refrigerant mixture studied in this work, the refractive indices of the pure components have comparable values [10–12]; thus, only the scattered light signals from temperature and pressure fluctuations, associated with the thermal diffusivity and speed of sound, respectively, may be resolved.

2.2 Surface Light Scattering

The method of surface light scattering (SLS) is very similar to that of light scattering from bulk fluids ("conventional" DLS). The major difference relies on the fact that, in SLS, fluctuations are analyzed on the surface of a liquid or, in general, on boundary layers between two different phases. Surface waves, whose energy quanta are referred to as "ripplons," form on interfacial boundary layers as a consequence of thermal molecular motion. For the case of low viscosity, as is relevant in the present investigations of a quaternary refrigerant mixture, the amplitude of the surface fluctuations decreases with time as a damped oscillation. To a first approximation, the frequency and damping of surface waves on a free liquid surface are determined by the liquid kinematic viscosity and surface tension, respectively. In SLS, scattered light emerging from the interaction between light and the fluctuating surface structure is analyzed. As in "conventional" DLS, this can be done through a temporal analysis of the scattered light intensity using photon correlation spectroscopy (PCS).

The kinematic viscosity of the liquid phase $\nu'(=\eta'/\rho')$ and the surface tension σ were determined under saturation conditions, within the scope of this work, by means of an exact numerical solution of the dispersion relation for surface waves. In addition to the information about the dynamics of the surface fluctuations obtained from the SLS experiment, reference data for the density of both phases and the dynamic viscosity of the vapor phase under saturation conditions were utilized for this purpose.

3 Experimental

The experimental setup, including the optical and electro-optical parts, the sample cell, and the thermostat, used here for the determination of thermal diffusivity and sound speed by "conventional" DLS is the same as that employed in our former investigations for numerous pure refrigerants and refrigerant mixtures; see, e.g. [2,8,13]. This same statement also holds for the determination of liquid kinematic viscosity and surface tension from SLS. Here, the reader is referred to [2,9,14].

In the following, only the experimental conditions for the present investigations of the quaternary refrigerant mixture R-125/143a/32/134a are stated. According to the specifications of the manufacturer (Solvay Fluor GmbH, Hannover), the refrigerant sample had a purity of ≥99.5 mass% and was used without further purification. The liquid mixture composition was analyzed by gas chromatography to be 21.0 mass% R125, 29.4 mass% R143a, 24.3 mass% R32, and 25.3 mass% R134a. The uncertainty in the mixture composition can be specified to be 0.2% for each component. For the present measurements, the sample was filled into an evacuated cylindrical pressure vessel ("conventional" DLS: volume $\approx 10\,\mathrm{cm}^3$; SLS: volume $\approx 150\,\mathrm{cm}^3$) from the liquid phase to avoid demixing, since the quaternary mixture R-125/143a/32/134a constitutes a non-azeotropic mixture. For this reason, investigations were restricted to the liquid phase and special experimental care was taken to maintain the mixture at the certified composition of the manufacturer for the complete temperature range investigated. In order to keep the change in composition to a minimum, the vapor space in the measuring cell had to be kept as small as possible.

The temperature of the pressure vessels, which were placed inside insulated housings, was regulated through resistance heating and measured by calibrated 25-Ω or 100-Ω platinum resistance probes with an uncertainty of 15 mK. The temperature stability was better than ±2 mK during each experimental run. For each temperature point, typically six single measurements were performed at different adjustments of the optical setup. In the SLS experiments, for temperatures below room temperature, the insulating housing was cooled by a lab thermostat to about 10 K below the desired temperature in the sample cell.

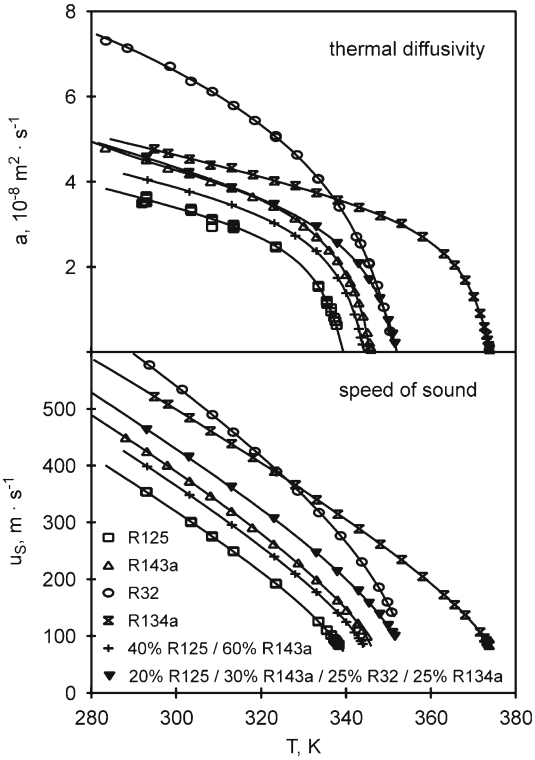

Fig. 1 Thermal diffusivity a (upper part) and sound speed u_S (lower part) of the saturated-liquid phase of a quaternary R-125/143a/32/134a refrigerant mixture as a function of temperature in comparison with the values of the pure components R125 [15], R143a [13], R32 [8,16], and R134a [17] and a binary refrigerant mixture R-125/143a [3]

4 Results and Discussion

4.1 Thermal Diffusivity and Sound Speed

The experimental data for the thermal diffusivity and sound speed of the quaternary refrigerant mixture in the saturated-liquid phase, obtained by light scattering from bulk fluids, are plotted in Fig. 1 and summarized in Table 1. In the figure, the closed and open symbols distinguish between the present data for the quaternary R-125/143a/32/134a mixture and that from previous investigations of a binary mixture of 40 mass% R125 and 60 mass% R143a [3] as well as for the pure components [8,13,15–17]. For the quaternary mixture, the symbols represent the mean value of up to six single measurements at different adjustments of the optical setup.

For the thermal diffusivity and sound speed, the measurement uncertainty is estimated to be less than 1 and 0.5%, respectively, except for a few data points close to the critical point. The evaluation of the uncertainties is based on the standard deviation of the single measurements, which may be regarded as a direct measure of the uncertainty of data by DLS from bulk fluids [18]. Approaching the critical point, an increasing

Table 1 Experimental values of the thermal diffusivity a and sound speed u_S of a quaternary R-125/143a/32/134a refrigerant mixture in the saturated-liquid phase (liquid mixture composition: 21.0 mass% R125, 29.4 mass% R143a, 24.3 mass% R32, and 25.3 mass% R134a)

T (K)	Thermal diffusivity a ($10^{-8}\,\mathrm{m}^2\cdot\mathrm{s}^{-1}$)	Sound speed u_S ($\mathrm{m}\cdot\mathrm{s}^{-1}$)
293.08	4.58	463.3
303.03	4.22	415.0
313.05	3.86	362.2
323.07	3.47	306.7
333.03	2.95	246.0
338.00	2.55	213.3
343.02	2.07	179.1
345.49	1.69	157.8
348.01	1.25	138.0
350.00	0.741	118.4
351.00	0.420	105.8
351.59	0.201	99.60

standard deviation for the thermal diffusivity and sound speed measurements of 2 and 1%, respectively, could be observed. This behavior can be attributed to the increasing experimental complexity in the critical region. Undeniably, the overall uncertainty of our mixture data, including the uncertainty in the composition, is somewhat larger. This effect could be estimated with the help of the simple prediction method, Eq. 1. For both thermal diffusivity and sound speed, the uncertainty in the composition may result in an additional uncertainty of up to about 0.1%.

The lines in Fig. 1 are empirical correlations of our experimental data. The thermal diffusivity and the sound speed can be well represented, within the experimental uncertainty, by a sum of a linear and an additional term, which takes into account the curvature to the critical point, resulting in an equation of the form

$$y = y_0 + y_1(T/K) + \frac{y_2}{(T - T_C^*)/K}, \tag{2}$$

where the coefficients y_i and the additional fit parameter T_C^* are given in Table 2. The root-mean-square deviations of our values from Eq. 2 and the ranges of validity are also stated. From the curvature of the empirical correlations of the pure components in Fig. 1, the fact that the quaternary mixture is made up of different types of components becomes apparent, with the curvature for R32, a methane derivative, being clearly different from that of the ethane derivatives R125, R143a, and R134a.

In the following, our primary interest is directed to the comparison of the experimental mixture data with the simple prediction method according to Eq. 1. Because this prediction approach is based on the properties of the pure-component data expressed as functions of the reduced temperature, its successful application not only requires information about the pure-component data but also an accurate knowledge

Table 2 Coefficients of Eq. 2

y_i	Thermal diffusivity a y_i ($10^{-8}\,\text{m}^2\cdot\text{s}^{-1}$)	Sound speed u_S y_i ($\text{m}\cdot\text{s}^{-1}$)
y_0	12.2994	1,852.97
y_1	−0.024908	−4.63477
y_2	29.6276	2,341.6
T_C^* (K)	360.4467	370.608
T-range (K)	293–352	293–352
rms (%)	0.85	0.65

of the mixture critical temperature. For the quaternary refrigerant mixture, the critical temperature was determined to be $T_C = 352.05\,\text{K} \pm 0.1\,\text{K}$ by extrapolating the experimental data for the thermal diffusivity to zero, which is true at the critical point. This value differs from that reported by the NIST reference data base (REFPROP) of $T_C = 351.27\,\text{K}$ [19] for the same system. For the pure components, the following critical temperatures were adopted from the literature: 339.40 K for R125 [20], 346.04 K for R143a [21], 351.45 K for R32 [22], and 374.18 K for R134a [23].

In Fig. 2, the experimental data for the thermal diffusivity and sound speed are compared with the results according to the simple prediction method, with error bars illustrating the measurement uncertainty of the DLS experiment, as previously described. In applying Eq. 1, the pure-component data for R125, R143a, R32, and R134a have been taken from earlier DLS measurements [8,13,15–17]. For the thermal diffusivity, the data predicted according to the prediction scheme based on mass weighting, Eq. 1, exhibit relatively large deviations from the experimental data, with typical values of about ±10%, as can be seen in the upper part of Fig. 2.

Aiming at a better prediction accuracy for the thermal diffusivity, further approaches were tested, e.g., by using simple mass or molar weighting of the pure-component data. In these cases, remarkable deviations appeared in the vicinity of the critical point, as already noticed for other systems of refrigerant mixtures. A deterioration of the prediction performance could also be observed when using the molar fraction, instead of the mass fraction, in Eq. 1, in which case the absolute average deviation of the measurement data from the prediction increased from 9.4 to 12.9%. In the present work, an alternative weighting strategy based on mass/molar mass weighting is proposed:

$$Y_M(T_R) = \sum_j \frac{w_j M_j}{\sum_k w_k M_k} Y_j(T_R), \tag{3}$$

where w_j and w_k are the mass fractions of the single components, M_j and M_k are their molar masses, and Y_j is the desired property for the pure components at the reduced temperature $T_R = T/T_C$. Having introduced only the molar mass of the pure components as an additional variable in Eq. 3, the characteristic simplicity of the prediction method is conserved. For the quaternary mixture, the thermal-diffusivity data could be predicted much more accurately by using Eq. 3, when compared to Eq. 1, with deviations of usually less than 5%, except in the vicinity of the critical

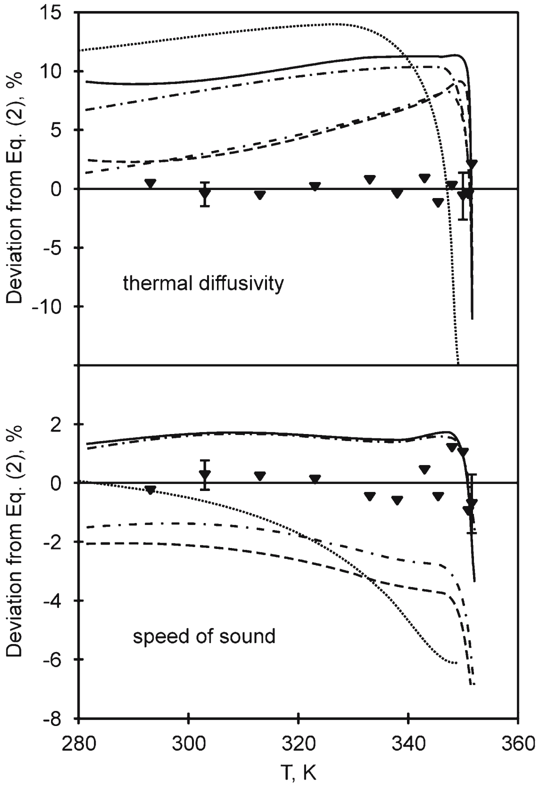

Fig. 2 Data comparison for the thermal diffusivity a (upper part) and sound speed u_S (lower part) of the saturated-liquid phase of a quaternary R-125/143a/32/134a refrigerant mixture: ▼, DLS-experiment; —, prediction from Eq. 1 using only pure-component data; -·-·, prediction from Eq. 1 treating R-125/143a as a pseudo-component; - - -, prediction from Eq. 3 using only pure-component data; - - ·, prediction from Eq. 3 treating R-125/143a as a pseudo-component; · · ·, REFPROP [19]

point, where deviations of up to approximately ±8% can be observed, see Fig. 2. The absolute average deviation of the experimental data from the prediction Eq. 3 is 6.0%, and thus clearly lower than the corresponding value resulting from the prediction according to Eq. 1. Not only did the mass/molar mass-weighted prediction method perform better for the thermal diffusivity of the quaternary mixture, but also when applied to other multicomponent systems. As shown in Fig. 3, the prediction scheme based on mass/molar mass weighting, Eq. 3, produces significantly better results for the thermal diffusivity of the saturated-liquid phase of all previously investigated mixtures (R507 [1], R404A [1], R410A [2], R407C [2], and R-125/143a [3]), with almost no exception, with factors of up to two between the deviations of both prediction methods from the experimental data for a given system.

As opposed to the thermal diffusivity, the sound speed in the saturated-liquid phase could be satisfactorily predicted with the simple prediction method based on mass weighting, Eq. 1, with deviations from the experimental data of less than ±3% over the whole temperature range studied, as can be seen in the lower part of Fig. 2. The

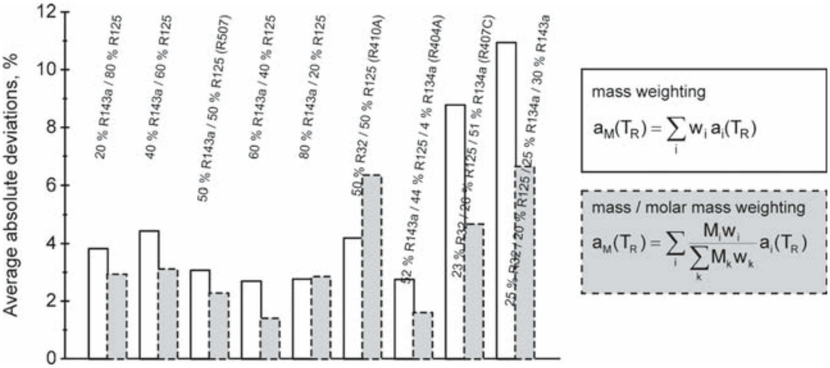

Fig. 3 Absolute average deviation of the data for the thermal diffusivity *a* of the saturated-liquid phase from the simple prediction using either mass weighting, Eq. 1, or mass/molar mass weighting, Eq. 3, for all mixtures investigated up to now by DLS (R507 [1], R404A [1], R410A [2], R407C [2], R-125/143a [3], and R-125/143a/32/134a)

absolute average deviation of the experimental speed-of-sound data from Eq. 1 is 1.3%. The introduction of the mass/molar mass-weighting strategy is thus not only unnecessary but also counterproductive in this case, resulting in deviations of more than −6% in the vicinity of the critical point.

Also evident in Fig. 2 appears the possibility of simplifying the simple prediction methods, Eqs. 1 and 3, through the introduction of so-called pseudo-components, which can be treated for prediction purposes as single components, but which in reality constitute a mixture, see Sect. 1. If the pseudo-component has been previously investigated at the corresponding concentration ratio in the mixture, as is the case for the R-125/143a binary at a ratio of 2 to 3 [3], single components can be substituted by pseudo-components in Eqs. 1 or 3, with almost no effect on the predicted property for the mixture, as it can be seen in Fig. 2 for the prediction of both thermal diffusivity and sound speed with the two different weighting strategies. Of course, when applying the concept of pseudo-components, their critical temperatures are also required. Here, for the pseudo-component consisting of 40 mass% R125 and 60 mass% R143a, a critical temperature of $T_C = 344.41$ K was used, originating from our former investigations [3]. The results arising from introducing pseudo-components not only constitute a mathematical simplification of the prediction method, but also ratify the validity of previous experimental investigations of mixtures with a lesser number of components.

In addition, a comparison of the predicted thermal diffusivity and sound speed of the studied quaternary mixture according to REFPROP [19] with our experimental data is presented in Fig. 2. For the thermal diffusivity, deviations of more than ±10% can be observed at practically all investigated temperatures, with values steeply increasing in the vicinity of the critical point, making the prediction according to REFPROP [19] more inaccurate than that resulting from the simple prediction method, Eqs. 1 and 3. For the sound speed, the prediction by REFPROP [19] exhibits deviations starting from almost negligible values at temperatures lower than about 300 K and quickly increasing to more than −6% as the critical point is approached, thus also being less accurate than the mass-weighted prediction method at higher temperatures, Eq. 1.

Table 3 Liquid kinematic viscosity ν' and surface tension σ of a quaternary R-125/143a/32/134a refrigerant mixture at saturation conditions (liquid mixture composition: 21.0 mass% R125, 29.4 mass% R143a, 24.3 mass% R32, and 25.3 mass% R134a)[a]

T (K)	η'' (μPa · s)	ρ' (kg · m^{-3})	ρ'' (kg · m^{-3})	ν' (mm^2 · s^{-1})	σ (mN · m^{-1})
243.15	10.0	1, 244.9	7.8	0.2104	13.28
253.15	10.5	1, 212.8	11.6	0.1923	11.88
263.15	10.9	1, 179.2	16.8	0.1731	10.41
273.15	11.3	1, 143.8	23.7	0.1613	9.00
283.15	11.7	1, 106.1	32.7	0.1468	7.56
293.15	12.1	1, 065.4	44.6	0.1364	6.20
303.15	12.7	1, 020.8	60.1	0.1259	4.94
313.15	13.4	970.8	80.7	0.1177	3.67
323.15	14.3	912.7	108.8	0.1077	2.50
333.15	15.6	841.1	149.6	0.0954	1.41
343.15	18.0	738.4	218.0	0.0841	0.481

[a] Directly measured values for frequency and damping at a defined wave vector of surface waves were combined with literature data for ρ', ρ'', and η'' according to [19] to derive ν' and σ by an exact numerical solution of the dispersion relation

The relatively large differences between the experimental data of this work and those predicted by REFROP [19] for both properties, especially in the vicinity of the critical point, may be partly attributed to the difference in the critical temperature reported by both sources. The value given by REFROP [19] differs from the value determined within this work, as previously discussed, by almost 0.8 K. For the thermodynamic properties, furthermore, the database's calculation model, which is based on the work of Lemmon and Jacobsen [24], was never tested for a quaternary mixture, but only for binary and ternary mixtures. In this context, it is possible that because of the limited data for the sound speed of binary mixtures of R32, R125, R134a, and R143a, additional measurements are needed in order to reduce the uncertainty of the database's calculation model [25].

4.2 Viscosity and Surface Tension

The results from SLS for the liquid kinematic viscosity and surface tension of the quaternary refrigerant mixture under saturation conditions are summarized in Fig. 4 and listed in Table 3. The mixture data represent average values of typically six independent measurements at different adjustments of the optical setup. In addition to the mixture data, the pure-component data, which are reported in [9], are shown in Fig. 4. It should be noted that the pure-component data from [9] represent recalculated data from the original work [14], in which an approximation was used for describing the dynamics of surface waves for data evaluation purposes.

In addition to the results for the kinematic viscosity and surface tension, Table 3 includes the reference data used for the data evaluation, see Sect. 2.2. The density

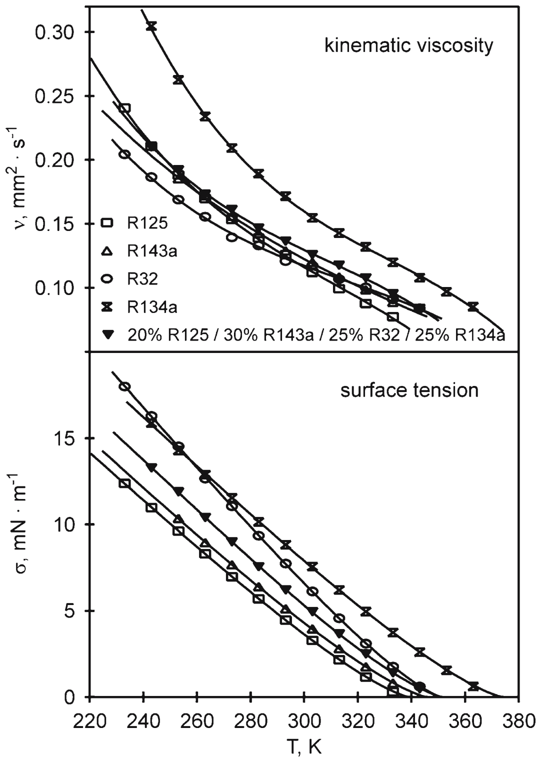

Fig. 4 Liquid kinematic viscosity ν' (upper part) and surface tension σ (lower part) under saturation conditions of a quaternary R-125/143a/32/134a refrigerant mixture as a function of temperature in comparison with the values of the pure components R125, R143a, R32, and R134a [9]

of the saturated-liquid and -vapor phases, ρ' and ρ'', respectively, and the dynamic viscosity in the saturated-vapor phase η'' were taken from REFPROP [19]. Taking into account the uncertainties of the individual quantities entering into the calculation, the uncertainty of our liquid kinematic viscosity data is estimated to be smaller than 1% for reduced temperatures $T_R<0.8$. The uncertainty is clearly worse at higher temperatures, yet for temperatures not too close to the critical point ($T_R < 0.95$), a reasonable uncertainty of less than 2% could be maintained. For the surface tension, the uncertainty is estimated to be smaller than 1.5%, except at the highest temperatures investigated. It should be noted that even approximate values for the dynamic viscosity of the vapor phase are sufficient to achieve such an accuracy. A more detailed discussion regarding the accuracy achievable for the liquid kinematic viscosity and surface tension from SLS can be found in [9,26]. For evaluation of the overall uncertainty of the present mixture data from SLS, the uncertainty in the composition has also been taken into consideration. By using the model given in Eq. 1, for both kinematic viscosity and surface tension, an additional uncertainty of up to about 0.1%, introduced by the uncertainty in the composition, could be estimated. In Fig. 5, error bars illustrate the discussed uncertainties for selected experimental data points.

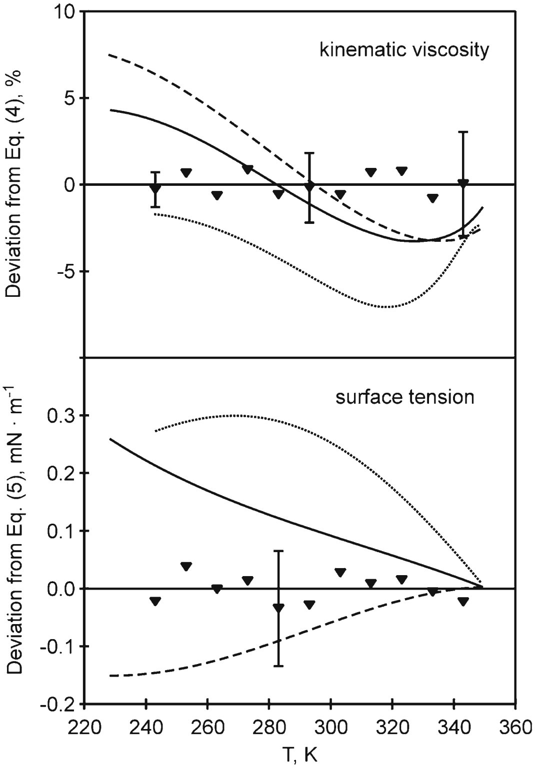

Fig. 5 Data comparison for the liquid kinematic viscosity ν' (upper part) and surface tension σ (lower part) under saturation conditions of a quaternary R-125/143a/32/134a refrigerant mixture: ▼, DLS-experiment; —, prediction from Eq. 1 using only pure-component data; - - -, prediction from Eq. 3 using only pure-component data; · · ·, REFPROP [19]

For the complete temperature range studied, an empirical description taking the form of a polynomial of third order was chosen

$$\nu' = \sum_{\mathrm{i}=0}^{3} \nu'_{\mathrm{i}} \left(T/K\right)^{\mathrm{i}}, \tag{4}$$

in order to represent the kinematic viscosity of the quaternary refrigerant mixture, where T is the temperature in K and the coefficients ν'_{i} are given in Table 4. Here, the standard deviation of our data relative to those calculated by Eq. 4 is also reported. It should be noted that the residuals of the experimental data from the fit are smaller than the standard deviations of the individual measurements, which were less than 1.0%.

The experimental data for the surface tension are represented by a modified van der Waals-type surface tension equation of the form [27]

$$\sigma = \sigma_0 \left(1 - T_{\mathrm{R}}\right)^{1.26} \left[1 + \sigma_1 \left(1 - T_{\mathrm{R}}\right)^{0.5} + \sigma_2 \left(1 - T_{\mathrm{R}}\right)\right], \tag{5}$$

Table 4 Coefficients of Eq. 4

ν'_0 $(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	3.12923
$\nu'_1 \times 10^2$ $(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	−2.727959
$\nu'_2 \times 10^5$ $(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	8.519178
$\nu'_3 \times 10^8$ $(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	−9.195796
rms (%)	0.61
T-range (K)	243–343

Table 5 Coefficients of Eq. 5

σ_0 $(\mathrm{mN} \cdot \mathrm{m}^{-1})$	54.167
σ_1	0.5957
σ_2	−0.8019
T_C (K)	351.27 [19]
rms (%)	1.40
T-range (K)	243–343

where the fit parameters σ_0, σ_1, and σ_2 are given in Table 5. This correlation uses a critical temperature of 351.27 K, adopted from REFPROP [19], and represents the experimental values of the surface tension with a root-mean-square deviation of 1.4%. A clearly larger value of about 2.7% would result if the critical temperature of 352.05 K was used in Eq. 5, as found from the extrapolation of our thermal diffusivity measurements, see Sect. 4.1. The fact that the density data needed for the evaluation of the SLS-measurements (see Sect. 2.2) was extracted from REFPROP [19] as well explains why the data correlation using the critical temperature from this source represents the experimental results more precisely.

As for the thermal diffusivity and sound speed, the simple prediction method using both mass and mass/molar weighting according to Eqs. 1 and 3, respectively, was used for predicting the kinematic viscosity and surface tension of the investigated quaternary mixture in its saturated-liquid phase. For this, the pure-component data have been taken from previous SLS measurements [9]. In the upper and lower parts of Fig. 5, the deviations of the predicted values from the experimental data correlations, Eqs. 4 and 5, are shown for the kinematic viscosity and surface tension, respectively. As opposed to the thermal diffusivity and sound speed, however, the critical temperature used for the prediction of both kinematic viscosity and surface tension was extracted not from the thermal-diffusivity data but from REFPROP [19], thus keeping it consistent with the data correlation for the surface tension described above.

From Fig. 5 it is evident that both kinematic viscosity and surface tension can be acceptably predicted with the simple prediction method using mass weighting, Eq. 1, with an absolute average deviation of the measurement data from the prediction of 2.2% for both properties, within the whole examined temperature range. While for the prediction of the kinematic viscosity, the maximum deviations from the experimental data are less than ±4%; for the surface tension the situation is somewhat worse. At the highest temperature studied in this work, the predicted surface tension exhibits a positive maximum deviation of 7.4% with respect to its corresponding experimental data point, which may be partly attributed to the density data used for the data evaluation. It is noteworthy that by setting the critical temperature to a value of 352.05 K, as determined by our thermal diffusivity data, no significant influence on the prediction of the kinematic viscosity could be observed, yet the prediction of the surface tension worsens by a factor of two, with regard to the absolute average deviation of the measured data from the predicted values.

The prediction with mass/molar mass weighting, Eq. 3, proved to have an inferior performance for the kinematic viscosity, with deviations of more than 7%, while improving the predicted data for the surface tension. For the latter, the deviation of the prediction from the experimental data point at the highest temperature could be reduced to 4.5% with this approach, in comparison with the mass weighting method Eq. 1, resulting in an absolute average deviation of only 1.4%. Although the prediction with mass/molar mass weighting, Eq. 3, is the most suitable to represent the surface-tension data for the quaternary refrigerant mixture, this statement does not hold, as in the case of the liquid thermal diffusivity, for all other mixtures investigated until now. For these, best agreement is found with the prediction based on mass weighting, Eq. 1.

Once again, the simple prediction method proposed performed better, compared to the results from REFPROP [19], when predicting the kinematic viscosity and surface tension of the quaternary refrigerant mixture, as can be observed in Fig. 5. Our experimental data exhibit an absolute average deviation from the database of 4.7% for the first and a corresponding value of 4.9% for the latter.

The pseudo-component concept discussed in Sect. 4.1 could not be introduced in this case due to the lack of experimental data available for the kinematic viscosity and surface tension of the quaternary mixture's subsystems.

5 Conclusions

For the quaternary R-125/143a/32/134a refrigerant mixture, the thermal diffusivity, sound speed, liquid kinematic viscosity, and surface tension have been investigated under saturation conditions over a wide temperature range from 243 K and up to the liquid–vapor critical point, constituting the first attempt of studying the thermophysical properties of a quaternary system by DLS. The results have been compared to an already presented prediction method based on the properties of the pure-component data, expressed as functions of the reduced temperature, which proved to be applicable, for the first time, to a multicomponent mixture consisting of different types of components. Once again, but this time only for the properties of sound speed, liquid viscosity, and surface tension, the best agreement with the simple prediction method was obtained by a mass-weighted sum of the pure-component data. For the thermal diffusivity, however, better results could be obtained by weighting with both mass fraction and molar mass, in a combined manner. The possibility of simplifying the prediction method through substitution of single mixture components by binary or ternary mixtures could be verified.

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