Fundamental equation of state correlation for hexamethyldisiloxane based on experimental and molecular simulation data

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ABSTRACT

An empirical fundamental equation of state correlation in terms of the Helmholtz energy is presented for hexamethyldisiloxane. The relatively small amount of thermodynamic data that is available in the literature for this substances is considerably extended by speed of sound measurements and numerical results for Helmholtz energy derivatives from molecular modeling and simulation. The speed of sound apparatus employed in this work is based on the pulse-echo technique and operates up to 150 MPa in the temperature range between 250 K and 600 K. The range of validity of the equation of state, based on laboratory data from literature and speed of sound data of this work, is from 270 K to 580 K and up to 130 MPa. Molecular simulation data are applied to extend the range of validity up to 1200 K and 600 MPa.

1. Introduction

In heat recovery systems, such as organic Rankine cycles (ORC), one important group of working fluids are siloxanes, which belong to the wider class of organo-silicone compounds. Among others, hexamethyldisiloxane (CAS No.: 107-46-0, $C_6H_{18}OSi_2$) appears to be a good candidate for becoming a widely employed working fluid for high temperature ORC processes. However, accurate thermodynamic data for siloxanes are a prerequisite for optimally designed processes.

Traditionally, thermodynamic properties obtained from experiments are summarized in different forms of empirical equations of state. Correlations of the fundamental equation of state (EOS) are particularly useful, because every thermodynamic equilibrium property can be expressed as a combination of derivatives of the thermodynamic potential in terms of which the EOS is explicit. However, a sufficient amount of thermodynamic data is a key factor when it comes to empirical EOS development.

For hexamethyldisiloxane a fundamental EOS was published by Colonna et al. [1] in 2006. Upon commission of our speed of sound measurement apparatus that is briefly described below, it was found that this model yields unreliable data for this property. In

fact, with up to 15%, these deviations were so large that we decided to develop a molecular interaction model to independently corroborate our experimental findings.

Since 2006, the amount of experimental data that is available for hexamethyldisiloxane has expanded, particularly through the work of Abbas [2], but it is still rather poor; additional data sets were generated in the present work by means of speed of sound measurement and molecular modeling and simulation.

In principle, molecular simulation alone could provide any thermodynamic data at any state point and it is more cost and time efficient than laboratory measurements. However, its predictive capability is limited by the quality of the underlying molecular interaction model. Although molecular interaction models are usually adjusted only to a small amount of experimental data, it is generally accepted that they can provide reasonably good predictions for other state points and properties that were not considered during their optimization. However, consistently good inter- and extrapolation ability cannot be guaranteed. Our previous experience with several substances indicated that satisfactory performance still can be expected with respect to predicting various Helmholtz energy derivatives in the homogeneous fluid region, even if the molecular model was optimized exclusively to experimental vapor—liquid equilibrium data [3—7]. Nevertheless, due to the inherent uncertainty of molecular models, experimental data are still essential for EOS development.

Acoustic measurements allow for a fast and convenient access to

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the speed of sound. In case of fluids, such measurements contribute substantially to the development and parameterization of EOS [8] because accurate speed of sound data can efficiently be obtained over a large range of temperature and pressure. The common measuring principle for determining the speed of sound of liquids is the pulse-echo technique, which was introduced by Kortbeek et al. [9]. In this method, sound waves, emitted by an excited quartz crystal, propagate through a fluid over a known propagation distance, are reflected and travel back to the quartz crystal. The interference and correlation approaches are common for the pulse-echo technique for determining the propagation time of the wave signal. Here, the correlation approach was employed for the speed of sound measurement.

2. Speed of sound measurement

2.1. Measurement principle

Speed of sound measurements were carried out with the pulse-echo technique. By emitting a high frequency modulated burst signal with a piezoelectric quartz crystal, which was positioned in the fluid between two reflectors with different path lengths l_1 and l_2, where $l_1 < l_2$, the speed of sound was determined by the time measurement of the signal propagation through the fluid over a known distance [10,11]. The speed of sound, neglecting dispersion and diffraction effects, is given by the ratio of the propagation distance and the propagation time

$$w = \frac{2(l_2 - l_1)}{\Delta t}. \tag{1}$$

The measurement of the propagation time difference Δt was based on the correlation method, which was also used by Ball and Trusler [12], combined with a signal enhancement by applying Fast Fourier Transformation (FFT) to the original echo signals [13,14].

The quartz crystal was excited with a burst of 20 cycles, typically with a voltage of 10 V peak-to-peak. Both echoes were sampled, stored to a computer by an oscilloscope (Agilent, DSO1022A) and identified via a threshold. On the basis of the time intervals where the signals exceeded the specified threshold, a significantly extended number of data points in the time interval Δt_e was marked around both echo maxima, starting at t_1 for the first echo and at t_2 for the second echo, cf. Fig. 1 (top).

Because the second echo is affected by greater attenuation due to the longer propagation distance than the first echo, the ratio of the maximum amplitudes of the first echo and the second echo had be determined. The resulting amplitude factor r, which depends on the fluid and its thermodynamic state, is required in the correlation approach to consider attenuation [12]. This was done here by multiplying the second echo, i.e. the signal data within Δt_e after t_2, with the amplitude factor to achieve the same maximum peak magnitude for both echoes, cf. Fig. 1 (center).

The correlation z overlays the signals of both echoes by

$$z(\Delta t) = \sqrt{\sum_{t_1}^{t_1 + \Delta t_e} [x(t) \cdot rx(t + \Delta t)]^2}, \tag{2}$$

where $x(t)$ refers to the echo amplitude at the time t. The time at the maximum of z is the measured propagation time difference Δt, cf. Fig. 1 (bottom).

2.2. Measurement procedure

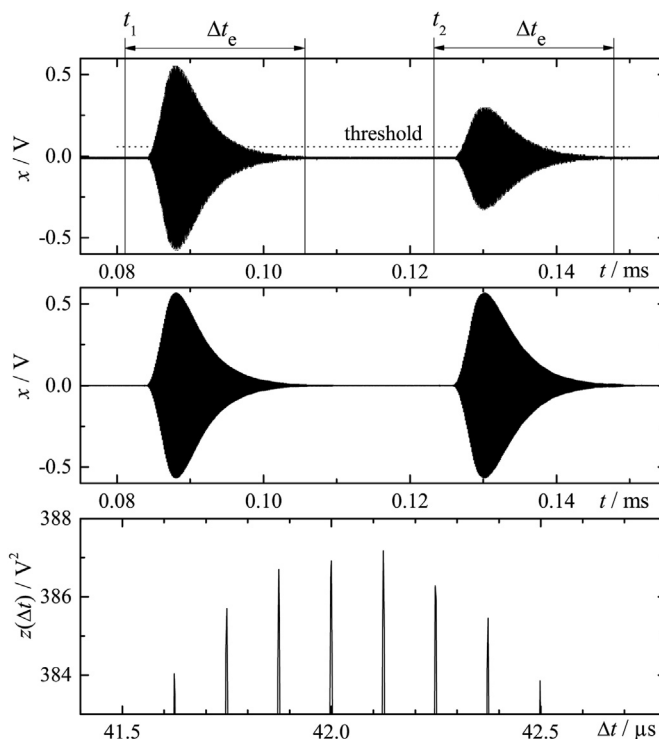After filling siloxane into the cell, it was compressed to about

Fig. 1. Steps of the correlation method. Top: First and second echo signals identified via a threshold. Center: Signal reconstructed by Fast Fourier Transformation where the amplitude of the second echo is the same as the amplitude of the first echo. Bottom: Correlation function $z(\Delta t)$ according to Eq. (2).

20 MPa by a hand-pump and an equilibration time of around 1 h was given to reach a constant pressure level. Each isotherm was studied from high pressure to vapor pressure, where the pressure was measured with a transducer (Honeywell TJE with an operating range up to 70 MPa), which was calibrated with a dead weight tester (Degranges and Hout, 5201-S) and protected by a blowout disc.

The temperature was measured with a Pt100 thermometer (Rössel Messtechnik RM-type), which was mounted in the wall of the pressure cylinder next to the quartz and was calibrated with a standardized 25 Ω platinum thermometer (Rosemount 162 CE). Hence, the overall uncertainty of the temperature measurement results according to the error propagation law due the individual uncertainty contributions amounts to $u_T = \pm 15$ mK.

For controlling the cell with a high accuracy over a wide temperature range, the thermostat was constructed with three nested copper shields. Each was monitored with respect to the temperature and equipped with one independently adjustable heater, which was controlled with a combination of a PID controller and an additional proportional (P) controller to quickly specify a constant temperature without overshooting.

The referencing of the path length distance difference $\Delta l = l_2 - l_1$ was carried out with water, which is available at high purity and for which highly accurate speed of sound measurements are available over a wide range of states, see Ref. [15]. The experimental speed of sound data were corrected by the diffraction correction by Harris [16], where significant dispersion effects are not expected for a resonance frequency of 8 MHz [17].

2.3. Results

Speed of sound measurements were carried out for a set of 12