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Research paper

Title:

Surface Tension of Low GWP Refrigerants R1243zf, R1234ze(Z), and R1233zd(E)

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Abstract

The surface tension of R1243zf, R1234ze(Z), and R1233zd(E) were measured at temperatures from 270 K to 360 K by an experimental apparatus based on the differential capillary rise method. The deviation between the measured surface tension of R134a and R245fa and the calculated surface tension with REFPROP 9.1 (Lemmon *et al.*, 2013) was $\pm 0.13 \text{ mN m}^{-1}$, which is less than the estimated propagated uncertainty in surface tension of $\pm 0.2 \text{ mN m}^{-1}$. Eleven points, thirteen points, and ten points of surface tension data were provided for R1243zf, R1234ze(Z), and R1233zd(E), respectively, in this paper. The measured data and the estimated surface tension using the methods of Miller (1963), Miqueu *et al.* (2000), and Di Nicola *et al.* (2011) agree within the standard deviation of $\pm 0.43 \text{ mN m}^{-1}$. The empirical correlations that represent the measured data within $\pm 0.14 \text{ mN m}^{-1}$ were proposed for each refrigerant.

Keywords : R245fa, R1234zf, R1234ze(Z), R1233zd(E), surface tension, capillary rise height

Nomenclature

N_A	Avogadro number	[-]
P	pressure	[MPa]
$[P]$	parachor	[-]
$STDEV$	standard deviation	[N m ⁻¹]
T	temperature	[K]
U	uncertainty in each parameter	[-]
V	molar volume	[cm ³ mol ⁻¹]
a^2	capillary constant	[m ²]

g	local gravitational acceleration	[m s ⁻²]
g_n	normal gravitational acceleration	[m s ⁻²]
h	capillary rise height	[m]
k	Boltzmann constant	[cm ² kg ⁻² K ⁻¹]
m	number of measured data	[-]
r	radius	[m]
t	reduced temperature	[-]

Greek letters

ω	acentric factor	[-]
θ	contact angle	[rad]
$\bar{\varepsilon}$	bias	[N m ⁻¹]
σ	surface tension	[N m ⁻¹]
σ_0	substance dependent parameter	[N m ⁻¹]
ρ'	orthobaric liquid density	[kg m ⁻³]
ρ''	orthobaric vapor density	[kg m ⁻³]

subscripts

1	capillary tube of the smaller diameter
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2 capillary tube of the larger diameter

b normal boiling point

c corrected

cal calculation

crit critical point

m measured

meas measurement

r reduced parameter

1. Introduction

Ozone depletion and global warming caused by refrigerants are currently a worldwide concern. In the last decade, great efforts have been made for alternatives to the conventional refrigerants R134a and R245fa with a 100-year time horizon global warming potential (GWP_{100}) of 1300 and 858 (Myhre *et al.*, 2013), respectively.

Brown *et al.* (2010) compared the estimated thermodynamic properties for eight hydro-fluoro-olefins (HFOs), namely, R1225ye(E), R1125ye(Z), R1225zc, R1234ye(E), R1234yf, R1234ze(E), R1234ze(Z), and R1243zf. Among these substances, the GWP_{100} of R1225ye(E), R1234yf, R1234ze(E), R1234ze(Z) and R1243zf were reported as less than 1 in IPCC 5AR (Myhre *et al.*, 2013). The newly developed blowing agent R1233zd(E) was recently nominated as the refrigerant or working fluid (Hulse *et al.*, 2012) alternatives to R245fa that is widely used in organic Rankine cycles. On the basis of the second law analysis, Cavallini *et al.* (2014) evaluated the performance potential of seven conventional refrigerants, three natural refrigerants (R600a, R290, and R717), and three hydro-fluoro-olefins (HFOs) (R1234yf, R1234ze(E), and R1234ze(Z)). Meanwhile, very comprehensive research has been conducted by McLinden *et al.* (2014). A set of 1200 low GWP refrigerants with critical temperatures between 300 K and 400 K was assessed, considering flammability, thermal stability, and toxicity for air conditioners. Nevertheless, the argumentation on the final candidate of low GWP refrigerant from a long-term prospective is still controversial.

The physical property data are necessary to build models to evaluate the efficiency and capacity of air conditioning and heat pump systems in which the candidate refrigerants are used. The surface tension is the one of important parameters that affects the heat transfer coefficient during condensation and evaporation. For R1234ze(E) and R1234yf, the surface tension data have been provided by Tanaka and Higashi (2013), Takahashi *et al.* (2009),

and Zhao *et al.* (2014). For R1233zd(E), only three points of surface tension data are reported by Hulse *et al.* (2012).

The measurement data of the other HFOs are not yet available in open literature at the present stage. Surface tension measurements were thus made for R1243zf, R1234ze(Z) and R1233zd(E) in this study.

2. Measurement

2.1 Measurement procedure and data reduction

Figure 1 shows an experimental apparatus for measuring the surface tension. The surface tension is measured as the capillary elevation in a small diameter tube immersed in a liquid. Two capillaries with inner radii of $r_1 = 0.4222 \pm 0.0009$ mm and $r_2 = 0.7526 \pm 0.0009$ mm are vertically set by a supporting brace in a pressure vessel (A) composed of a Pyrex glass tube that is 17 mm in inner diameter and 25 mm in outer diameter. The capillary radii were precisely measured with mercury slugs. These capillaries and pressure vessel are carefully cleansed by using an alkaline aqueous solution and an ultrasound bath in the preparatory procedure. The liquid of the test refrigerant is filled roughly to a half volume of the pressure vessels at room temperature. Then, the pressure vessel is placed in a thermostatic bath (B), and the temperature in the thermostatic bath is kept constant with a fluctuation within ± 2 mK using a main heater (J) and a PID (F) controlled sub heater (K). The temperature is measured with a 100Ω platinum resistance thermometer (C), ASL model F500, calibrated against ITS-90. The uncertainty of the temperature measurement is estimated to be within ± 5 mK. At steady state, the capillary rise difference between the two capillary tubes is measured using a digital travelling microscope (M) with a tolerance of 0.01 mm.

Figure 2 illustrates the differential capillary-rise-height. Specifically, with the travelling microscope and a CCD

camera (N), the height difference of the bottom of the meniscus in each capillary tube, Δh_m as shown in Figure 2, is measured. Figure 3 is the CCD image displayed on the monitor (G) to determine the position of the meniscus bottom. The differential height is read twice by six people (12 times reading in total) to eliminate the individual reading variation. The two standard deviations of 12 times readings was 0.046 mm. This deviation is taken into account as the reading error in the differential height measurement. The contact angle θ , shown in Figure 2, is approximated as zero. To obtain the actual differential capillary rise height, the measured differential height Δh_m at the bottom of the meniscus in each capillary tube has to be corrected by a methodology of Rayleigh (1916).

$$\begin{aligned}\Delta h_c &= (h_{m1} - h_{m2}) + \frac{(r_1 - r_2)}{3} - 0.1288 \left(\frac{r_1^2}{h_{m1}} - \frac{r_2^2}{h_{m2}} \right) + 0.1312 \left(\frac{r_1^3}{h_{m1}^2} - \frac{r_2^3}{h_{m2}^2} \right) + \dots \\ &= \Delta h_m + \frac{(r_1 - r_2)}{3} + O(r^2) \quad \text{at } r_1 < r_2\end{aligned}\tag{1}$$

where the remainder term $O(r^2)$ is $-0.012 \times 10^{-3} \text{ m} < O(r^2) < 0.022 \times 10^{-3} \text{ m}$ at $1 \times 10^{-3} \text{ m} < h_{m1} < 20 \times 10^{-3} \text{ m}$ and $1 \times 10^{-3} \text{ m} < h_{m2} < 20 \times 10^{-3} \text{ m}$. Because this remainder term is smaller than the reading error in the differential height, it is justified that the term is omitted in the correction. Therefore, the actual differential capillary-rise-height can be expressed as,

$$\Delta h_c \approx \Delta h_m + \frac{(r_1 - r_2)}{3}\tag{2}$$

The capillary constant a^2 is determined only from the capillary radii r_1 and r_2 , and the differential capillary-rise-height Δh_c ,

$$a^2 = \frac{g \Delta h_c}{g_n (1/r_1 - 1/r_2) \cos \theta} \approx \frac{g \Delta h_c}{g_n (1/r_1 - 1/r_2)}\tag{3}$$

where g and g_n are the local gravitational acceleration 9.8001 m s^{-2} at Iwaki, Japan and the normal gravitational accelerations 9.80665 m s^{-2} , respectively. The contact angle θ of refrigerants in the capillary tube, which is well

cleansed, is assumed zero. Hence, $\cos\theta$ is nearly equal to 1. The capillary constant is rewritten with the surface tension σ as,

$$a^2 = \frac{2\sigma}{g_n(\rho' - \rho'')} \quad (4)$$

The surface tension σ are determined from the capillary radii r_1 and r_2 , the differential capillary-rise-height Δh_c , and the orthobaric densities, ρ' and ρ'' .

$$\sigma = \frac{g\Delta h_c(\rho' - \rho'')}{2(1/r_1 - 1/r_2)\cos\theta} \approx \frac{g\Delta h_c(\rho' - \rho'')}{2(1/r_1 - 1/r_2)} = \left[\frac{gr_1r_2}{2(r_2 - r_1)} \Delta h_m - \frac{gr_1r_2}{6} \right] (\rho' - \rho'') \quad (5)$$

Heide (1997) used the exact same equation for his data reduction and validated this. The orthobaric densities, ρ' and ρ'' , are calculated from measured temperature with REFPROP 9.1 (Lemmon *et al.*, 2013) for R134a, R245fa, and R1233zd(E). For the refrigerants R1243zf and R1234ze(Z), fluid files optimized by Akasaka *et al.* (2015, 2014) from the measurement data provided by Higashi *et al.* (2015, 2014) were used to calculate ρ' and ρ'' associated with REFPROP 9.1.

The tested R1234ze(Z) and R1233zd(E) were supplied from Central Glass Co., Ltd., Japan. Preliminarily, they were well distilled, and the impurities were checked by a TCD gas chromatograph. These impurities were less than 0.1% by mole, which is within the uncertainty of the gas chromatograph. The sample of R1243zf used in this study was supplied from Mexichem, Ltd., UK. The purity of the supplied R1234zf is more than 99.5 % according to the manufacturer and the sample was used without further purification.

Table 1 lists the measurement uncertainties of the equipment mentioned above. The propagated uncertainty in surface tension is calculated by means of the square-root rule using the listed uncertainties. The calculation procedure for the uncertainty will be specified in Appendix A. The reading error in the capillary rise height was most dominant

in the propagated uncertainty. Typically, the propagated uncertainty is estimated to be within $\pm 0.2 \text{ mN m}^{-1}$.

2.2 Validity assessment for the measurement method

The reproducibility and repeatability of the above mentioned measurement methods were confirmed with R134a for the medium temperature refrigerant R1243zf having the critical temperature below 400 K and with R245fa for the high temperature refrigerants R1234ze(Z) and R1233zd(E) having the critical temperatures above 400 K. Figures 4 (a) and 4 (b) compare the surface tension between the present data and other data in literature for R134a and R245fa, respectively. For R134a, the measured surface tension provided by Chae *et al.* (1990), Heide (1997), Higashi *et al.* (1992), Higashi *et al.* (1997), and Zhu *et al.* (1993), and also the calculated surface tension by REFPROP 9.1 were compared in Figure 4 (a). For R245fa, the data provided by Schmidt *et al.* (1996), Lin *et al.* (2003), Zhelezny *et al.* (2007), and Geller *et al.* (1999), and also the calculated surface tension were compared in Figure 4 (b). REFPROP 9.1 adopts the correlations proposed by Mulero *et al.* (2012). The present surface tension data agree well with the calculated surface tension and selected data for R134a and R245fa. As shown in Figure 4 (b), data series 1 and 2 measured on the different days repeated along the calculated values. Figure 4 (c) plots the deviation of the present data from the calculated surface tension by using REFPROP 9.1. The standard deviation of 16 data was 0.13 mN m^{-1} , which is within the uncertainty 0.2 mN m^{-1} . As remarked, it was confirmed that the measurement method is sufficiently reproducible and repeatable.

3. Results and discussion

3.1. Measurement results

Table 2 provides the measured capillary constants a^2 given by Eq. (3) and the surface tensions σ given by Eq. (5) for R1243zf, R1234ze(Z), and R1233zd(E). The measured temperature T , calculated densities ρ' and ρ'' , corrected capillary rise height Δh_c , and uncertainty in surface tension U_σ are listed in Table 2 as well.

Figures 5 (a), 5 (b), and 5 (c) plot the measured surface tension as a function of temperature for R1243zf, R1234ze(Z), and R1233zd(E), respectively. The circle symbols indicate the present data; the small vertical bars overlapped with the symbols indicate the measurement uncertainty in surface tension. The diamond symbols are the critical temperatures T_{crit} , which are measured by Higashi *et al.* (2015) for R1243zf, Higashi *et al.* (2014) for R1234ze(Z) and by Hulse *et al.* (2012) for R1233zd(E). The triangle symbols in Figure 5 (b) are data for R1233zd(E) surface tension measured by Hulse *et al.* (2012). As seen in Figure 5 (b), the present data exhibits an approximately 1.5 mN m⁻¹ greater value than their data at a given temperature. For R1243zf and R1234ze(Z), no available measurement data can be found as of now.

3.2 Comparison with estimation methods

The present measurement data are compared with the estimation methods below. It should be noted that the methods are transcribed for the units N m⁻² and MPa.

i) Estimation based on the parachor, Macleodo(1923)-Sugden (1924) with modification by Fishtine (1963):

$$\sigma = ([P]\rho'_b)^4 \left(\frac{1-T_r}{1-T_{br}} \right)^{4n} \times 10^{-3} \quad (6)$$

$4n = 1.22$ (recommended between 1.0 and 1.24)

where ρ'_b is the molar liquid density at the normal boiling point in mol cm⁻³; $T_r \equiv T/T_{crit}$ is the reduced temperature;

while $T_{br} \equiv T_b / T_{crit}$ is the reduced normal boiling point. $[P]$ is a temperature independent parameter characteristic of a substance, called parachor. The values of parachor $[P]$ are listed in Table 3.

ii) Estimation based on the principle of corresponding states, Miller (1963):

$$\begin{aligned} \sigma &= (10 \times P_{crit})^{2/3} T_{crit}^{1/3} (1 - T_r)^{1/9} (Q \times 10^{-3}) \\ Q &= 0.1196 \left[1 + \frac{T_{br} \ln(P_{crit}/1.01325)}{1 - T_{br}} \right] - 0.279 \end{aligned} \quad (7)$$

where P_{crit} and T_{crit} are the critical pressure in MPa and temperature in K, respectively.

iii) Estimation based on the extended scaled equation, Miqueu *et al.* (2000):

$$\begin{aligned} \sigma &= k T_{crit} \left(\frac{N_A}{V_{crit}} \right)^{2/3} (4.35 + 4.14\omega) t^{1.26} (1 + 0.19t^{0.5} - 0.25t) \\ t &\equiv 1 - T/T_{crit} \end{aligned} \quad (8)$$

where k , N_A , V_{crit} , and ω are the Boltzmann constant in $\text{cm}^2 \text{kg s}^{-2} \text{K}^{-1}$, Avogadro number, critical volume in $\text{cm}^3 \text{mol}^{-1}$, and acentric factor, respectively.

iv) Estimation based on the extended scaled equation, Di Nicola *et al.* (2011):

$$\sigma = 0.658 (10 \times P_{crit})^{0.618} T_{crit}^{0.340} (1 + \omega)^{0.770} (1 - T_r)^{1.262} \times 10^{-3} \quad (9)$$

where P_{crit} and T_{crit} are the critical pressure in MPa and critical temperature in K. $T_r \equiv T/T_{crit}$ is the reduced temperature. ω is the acentric factor.

Figures 5 (a), 5 (b), and 5 (c) plot the estimated surface tension by the selected method with lines. As seen, the estimated value by the method of Macleodo-Sugden (Macleodo, 1923; Sugden, 1924) is distinctly greater than that

of the other estimations and present data. For R1243zf, the measured surface tension and the estimated surface tension by the methods of Miller (1963), Miqueu *et al.* (2000), and Di Nicola *et al.* (2011) are in good agreement. Most of the R1234ze(Z) data agree with these estimations within the measurement uncertainty 0.2 mN m^{-1} . In the case of R1234ze(Z), as shown in Figure 5 (b), the estimated values by Miqueu *et al.* (2000) slightly deviate from those by Miller (1963) and Di Nicola *et al.* (2011). The value of present data seems to agree with the estimations by Miller (1963) and Di Nicola *et al.* (2011) rather than that by Miqueu *et al.* (2000). In contrast, for R1233zd(E), the present data are somewhat greater than the estimated values and are close to the estimations by Miqueu *et al.* (2000) rather than those by Miller (1963) and Di Nicola *et al.* (2011).

To quantify the deviations, the following index bias $\bar{\varepsilon}$ and standard deviation *STDEV* are employed.

$$\bar{\varepsilon} = \frac{1}{m} \sum_{j=1}^m \varepsilon_j = \frac{1}{m} \sum_{j=1}^m (\sigma_{\text{cal},j} - \sigma_{\text{meas},j}) \quad (10)$$

$$STDEV = \sqrt{\frac{1}{m-1} \sum_{j=1}^m (\varepsilon_j - \bar{\varepsilon})^2} \quad (11)$$

where σ_{cal} and σ_{meas} denote the estimated and measured surface tensions, respectively. m is the number of measured data. Table 4 lists the indexes of the selected estimation method for the tested refrigerants. The Macleodo-Sugden method (Macleodo, 1923) estimates greater values. Especially for R1233zd(E), the bias indicates $+2.0 \text{ mN m}^{-1}$, which is considerably greater than the measurement uncertainty. Regarding the other three methods, the bias is within the measurement uncertainty for R1243zf. For R1234ze(Z), although the method of Miqueu *et al.* (2000) estimates a 0.7 mN m^{-1} greater value, the other two methods of Miller (1963) and Di Nicola *et al.* (2011) agree almost within the uncertainty. On the other hand, these three methods estimate a smaller surface tension, which is from -0.25 mN m^{-1} to -0.51 mN m^{-1} . The possible causes are the unexpected effects of chlorine on the measurement or the estimation,

the uncertainty in the critical parameters or the acentric factor. The standard deviation that indicates the scatterings is comparable to the measurement uncertainty for Miller (1963) and Di Nicola *et al.* (2011). The method of Miqueu *et al.* (2000) exhibits a slightly greater standard deviation because this method shows different relativity to the measured surface tension for each refrigerant. Nevertheless, the surface tension deviation of, for instance, 0.3 mN m⁻¹, differs the pool boiling heat transfer coefficient by only 0.4% for R1234ze(Z) at a reduced temperature of 74%, according to the correlation of Stephan and Abdelsalam (1980). Overall, the estimation methods of Miller (1963), Miqueu *et al.* (2000), and Di Nicola *et al.* (2011) should be sufficiently accurate for heat exchanger design.

3.3 Empirical correlation

For this situation, a more accurate surface tension estimation is required, the empirical correlation is proposed here. The solid lines in Figures 5 (a) and 5 (b) denote the empirical correlation, which are proposed with the following function form of the van der Waals equation.

$$\sigma = \sigma_0 \left(1 - T/T_{\text{crit}}\right)^n \quad (12)$$

where σ , T , and T_{crit} are the surface tension in N m⁻¹, temperature in K, and the critical temperature in K, respectively.

The coefficient σ_0 and the exponent n are optimized to fit the measured surface tension and the provided critical temperature by the least square mean method. From the principle of the corresponding state, the exponent n has been derived as 1.22 (= 11 / 9) by Guggenheim (1945) and verified by Brock and Bird (1955). This exponent shall range from 1.2 to 1.3 for most non-polar fluids (Reid *et al.*, 1987). According to the scaling law (Widom, 1974), this exponent is given as $n = 2\nu$ in three dimensions. The critical exponent ν is suggested 0.64 in his paper; however,

the number 0.63 is most authorized nowadays (Moldover, 1985). The correlations empirically obtained from the measurement data are summarized as,

$$\begin{cases} \sigma = 0.05330(1-T/376.93)^{1.247} [\text{N m}^{-1}] & \text{for R1243zf} \\ \sigma = 0.05657(1-T/423.27)^{1.220} [\text{N m}^{-1}] & \text{for R1234ze(Z)} \\ \sigma = 0.06195(1-T/438.75)^{1.277} [\text{N m}^{-1}] & \text{for R1233zd(E)} \end{cases} \quad (13)$$

The exponents in the empirical correlations Eq. (13) are close to the suggested number in previous studies. Figure 6 plots the deviation of the measured surface tension from the empirical correlation. As shown in Figure 6, these empirical correlations represent the measured surface tension within 0.13 mN m^{-1} and are available at temperatures from 270 K to 360 K.

3.4 Comparison with other refrigerants

Figure 7 compares the temperature dependence in surface tension between several refrigerants. Because the high temperature refrigerants have critical temperatures above 400 K, R1233zd(E), R245fa, and R1234ze(Z) are plotted. Because the medium temperature refrigerants have critical temperatures below 400 K, R134a and R1243zf are plotted. Additionally, the data of R1234ze(E), which is the isomer of R1234ze(Z), measured by Tanaka and Higashi (2013) are plotted. Comparing the surface tension between R1234ze(E) and R1234ze(Z) at a given temperature, the surface tension of R1234ze(Z) having a cis arrangement is markedly greater than that of R1234ze(E) having a trans arrangement. Although their constituent atoms and molecular weights are the same, most likely, the stronger polarity in the cis arrangement of R1234ze(Z) strengthens the surface tension. The surface tension gradient against the temperature of the HFO refrigerants R1233zd(E) and R1234ze(Z) having a carbonate double bond are comparable; meanwhile, the gradient of the HFC refrigerant R245fa is slightly greater than those of R1233zd(E) and R1234ze(Z).

Similarly, the gradient of the HFC refrigerant R134a is slightly greater than those of HFO refrigerants R1234ze(E) and R1243zf. Although the critical temperature of R1243zf is higher than that of R134a, the surface tension of R1243zf exhibits a smaller surface tension at temperatures below 340 K. Among the selected refrigerants, the temperature dependence in surface tension is more moderate for HFO refrigerants having a carbon double bond.

4. Conclusions

The surface tension data of low GWP refrigerants R1243zf, R1234ze(Z), and R1233zd(E) have been measured at temperatures from 270 K to 360 K by the differential capillary rise method. The measurement method was validated with conventional refrigerants R134a and R245a. The estimation method of Miller (1963), Miqueu *et al.* (2000), and Di Nicola *et al.* (2011) agreed with the measurement results within ± 0.43 mN m⁻¹. The empirical correlations with the function form of van der Waals equation were proposed as, $\sigma = 0.05330(1-T/376.93)^{1.247}$ for R1243zf, $\sigma = 0.05657(1-T/423.27)^{1.220}$ for R1234ze(Z), and $\sigma = 0.06195(1-T/438.75)^{1.277}$ for R1233zd(E), where σ and T are the surface tension in N m⁻¹ and the temperature in K, respectively. The correlation represents the measured surface tension within 0.13 mN m⁻¹.

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A. Uncertainty analysis

The measurement uncertainty in surface tension is specified here. The 95% coverage of uncertainty propagated with several variables is obtained by means of the square-root rule (Taylor 1982; Moffat, 1988), assuming that the variables are independent and random.

The uncertainty in the corrected differential capillary-rise-height Δh_c is considered to be same as that of the reading error 0.046 mm as listed in Table 1. Hence, from Equation (4), the uncertainty in surface tension can be expressed as,

$$U_{\sigma}^2 = \left(\frac{\partial \sigma}{\partial \rho''}\right)^2 U_{\rho''}^2 + \left(\frac{\partial \sigma}{\partial \rho'}\right)^2 U_{\rho'}^2 + \left(\frac{\partial \sigma}{\partial \Delta h_c}\right)^2 U_{\Delta h_c}^2 + \left(\frac{\partial \sigma}{\partial r_1}\right)^2 U_{r_1}^2 + \left(\frac{\partial \sigma}{\partial r_2}\right)^2 U_{r_2}^2 \quad (\text{A.1})$$

where

$$\left(\frac{\partial \sigma}{\partial \rho''}\right) = \frac{g \Delta h_c}{2(1/r_1 - 1/r_2)} \quad (\text{A.2})$$

$$\left(\frac{\partial \sigma}{\partial \rho'}\right) = \frac{g \Delta h_c}{2(1/r_1 - 1/r_2)} \quad (\text{A.3})$$

$$\left(\frac{\partial \sigma}{\partial \Delta h_c}\right) = \frac{g(\rho' - \rho'')}{2(1/r_1 - 1/r_2)} \quad (\text{A.4})$$

$$\left(\frac{\partial \sigma}{\partial r_1}\right) = -\frac{g \Delta h_c (\rho' - \rho'')}{2r_1^2 (1/r_1 - 1/r_2)^2} \quad (\text{A.5})$$

$$\left(\frac{\partial \sigma}{\partial r_2}\right) = \frac{g \Delta h_c (\rho' - \rho'')}{2r_2^2 (1/r_1 - 1/r_2)^2} \quad (\text{A.6})$$

The value of the each uncertainty source is listed in Table 1. The most dominant source is the reading error in the differential capillary-rise-height $U_{\Delta h_m} \approx U_{\Delta h_c}$. The estimated uncertainty in the surface tension U_{σ} ranges from 0.14 mN m⁻¹ to 0.30 mN m⁻¹.

Figure Captions

Figure 1 Experimental apparatus

Figure 2 Principle of differential capillary rise method

Figure 3 CCD image for the determination of meniscus bottom height

Figure 4 Validation of measurement method with R134a and R245fa

(a) Comparison on R134a surface tension data

(b) Comparison on R245fa surface tension data

(c) Deviation of the measured data from REFPROP 9.1

Figure 5 Temperature dependence in surface tension

(a) R1243zf

(b) R1234ze(Z)

(c) R1233zd(E)

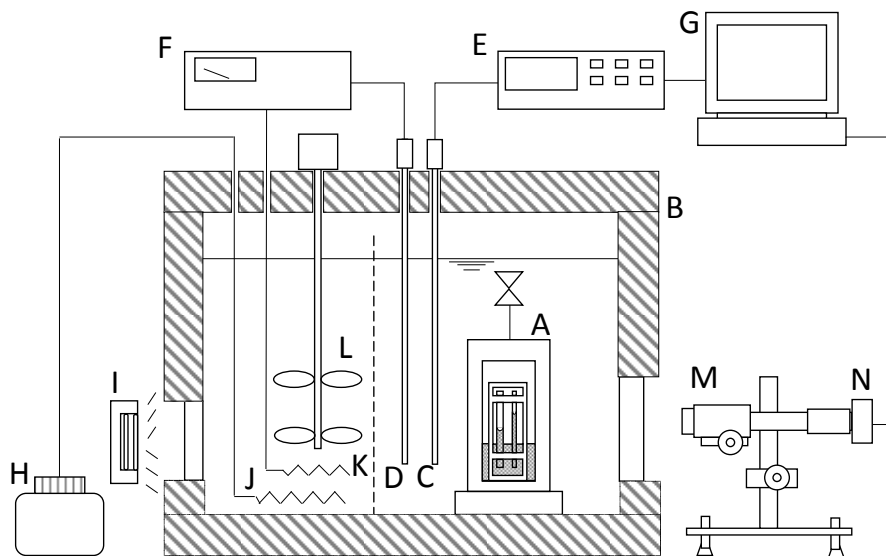
Figure 6 Temperature dependence in surface tension

(a) R1243zf

(b) R1234ze(Z)

(c) R1233zd(E)

Figure 7 Comparison of surface tension between refrigerants



- | | |
|--|-------------------------|
| A: pressure vessel | H: voltage transformer |
| B: thermostatic bath | I: illumination lamp |
| C: platinum resistance thermometer (100 Ω) | J: main heater (1 kW) |
| D: sheathed thermocouple | K: sub heater (500 W) |
| E: thermometer bridge | L: stirrer |
| F: temperature control system (PID) | M: traveling microscope |
| G: computer | N: CCD camera |

Figure 1 Experimental apparatus

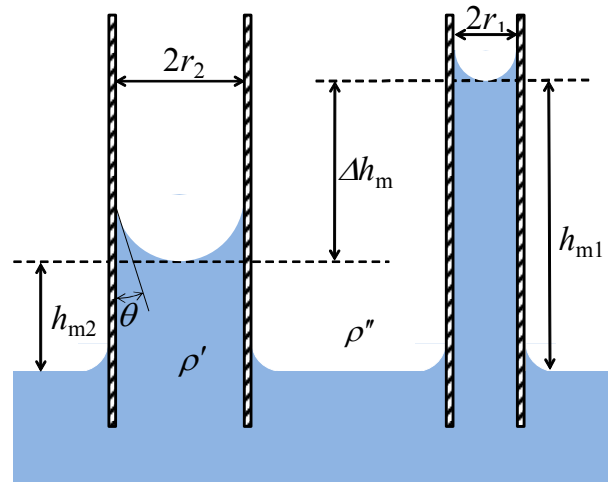


Figure 2 Principle of differential capillary rise method

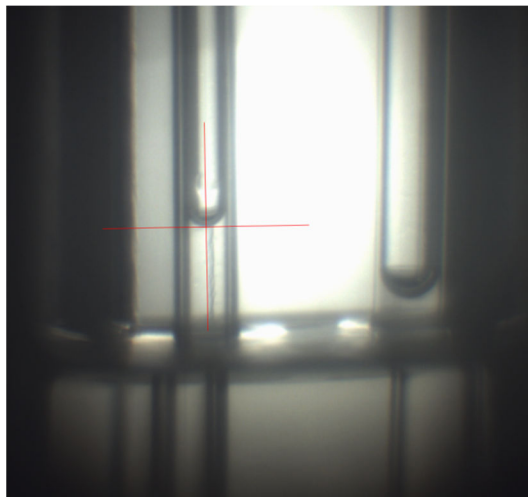
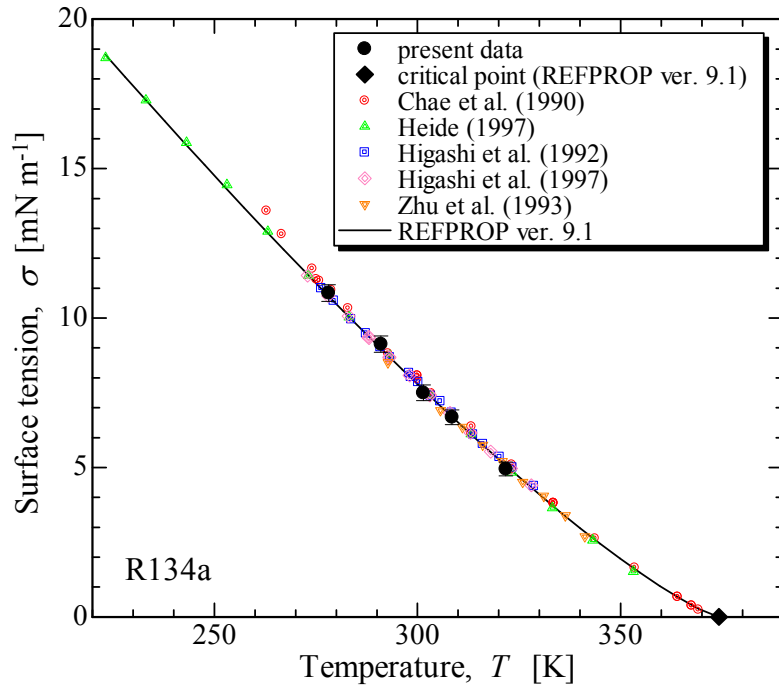
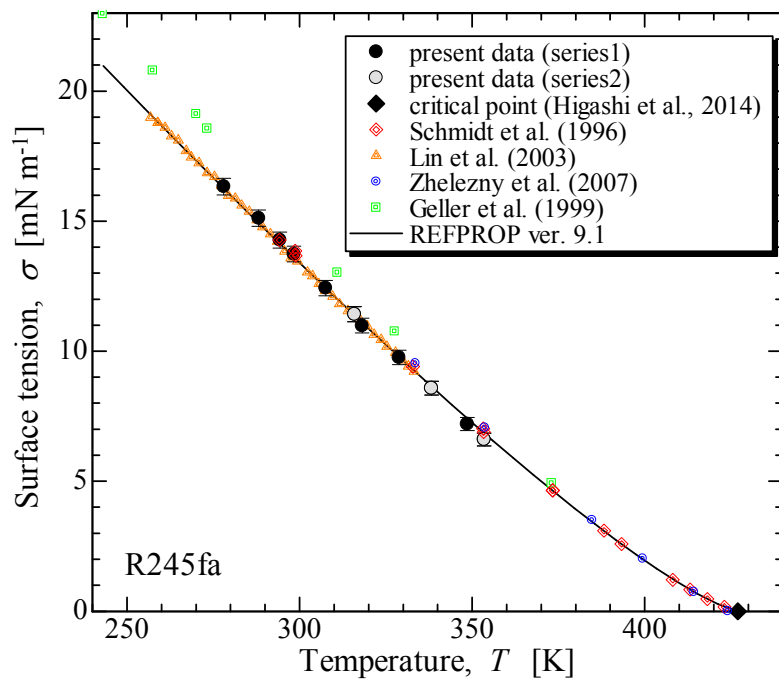


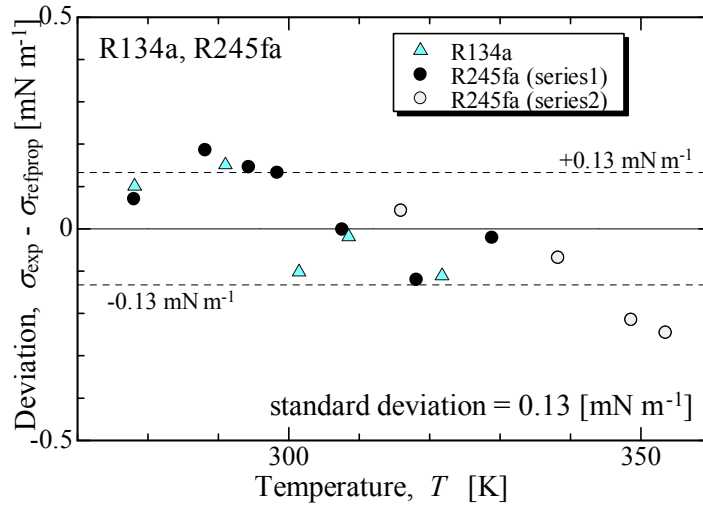
Figure 3 CCD image for the determination of meniscus bottom height



(a) Comparison on R134a surface tension data

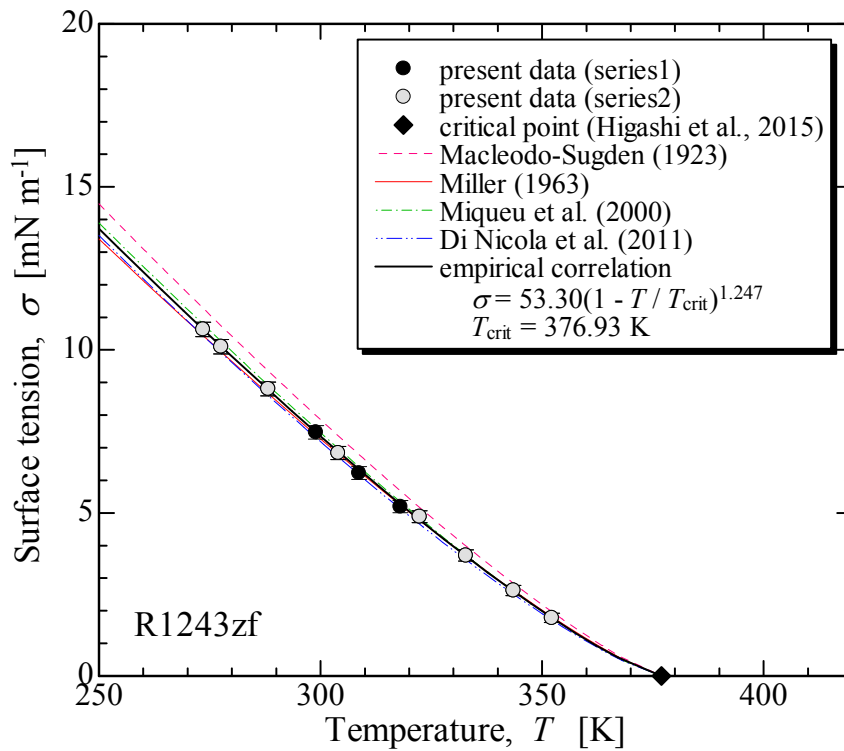


(b) Comparison on R245fa surface tension data

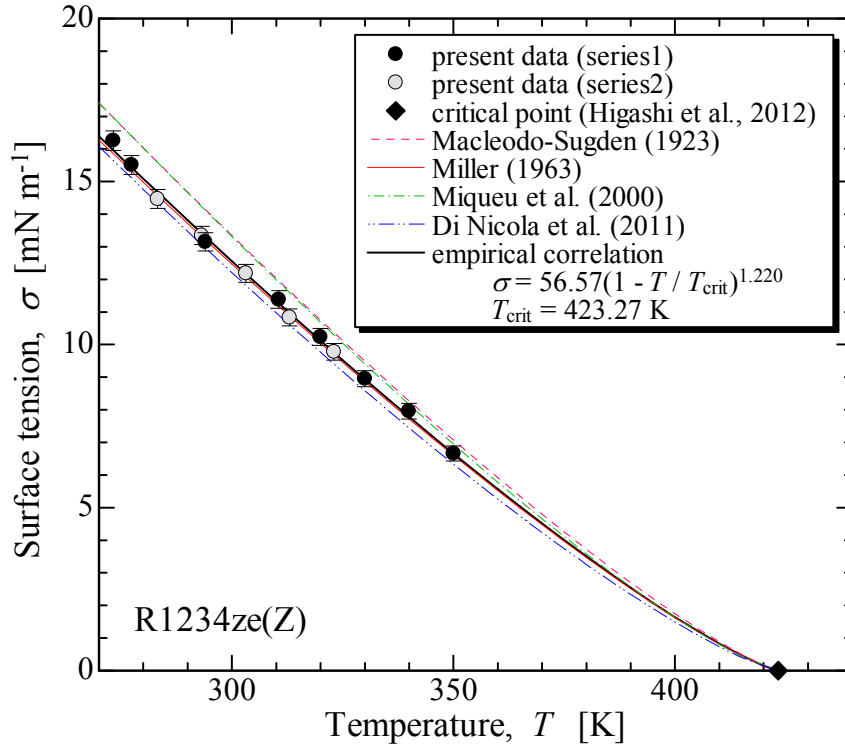


(c) Deviation of the measured data from REFPROP 9.1

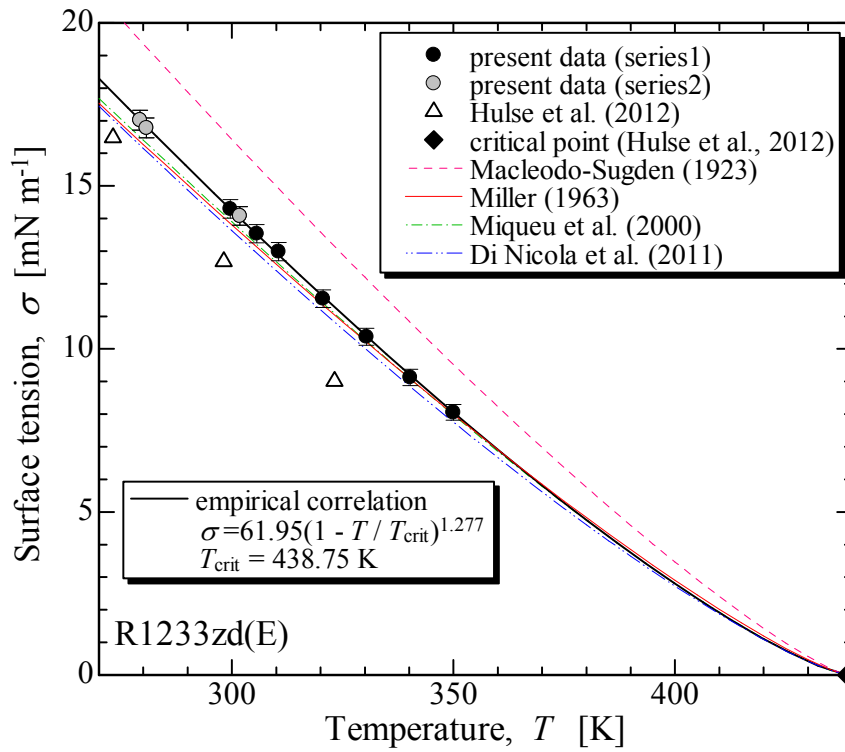
Figure 4 Validation of measurement method with R134a and R245fa



(a) R1243zf

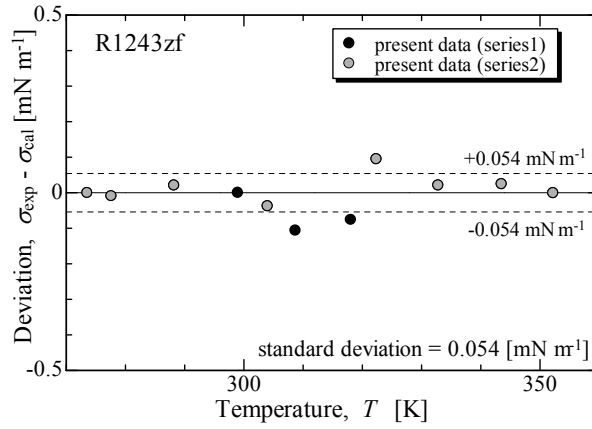


(b) R1234ze(Z)

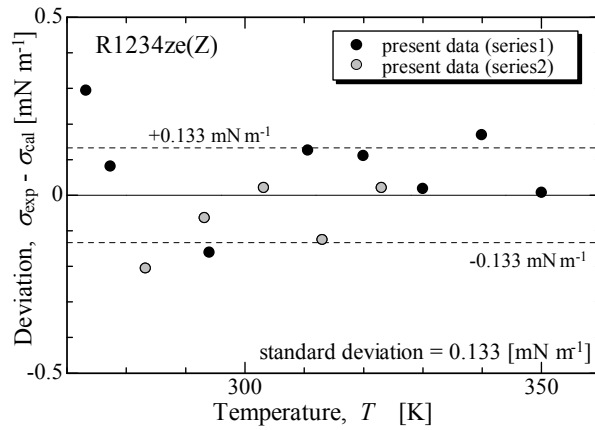


(c) R1233zd(E)

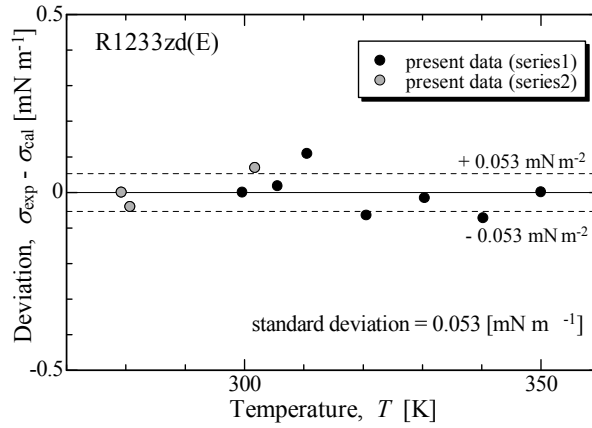
Figure 5 Temperature dependence in surface tension



(a) R1243zf



(b) R1234ze(Z)



(c) R1233zd(E)

Figure 6 Temperature dependence in surface tension

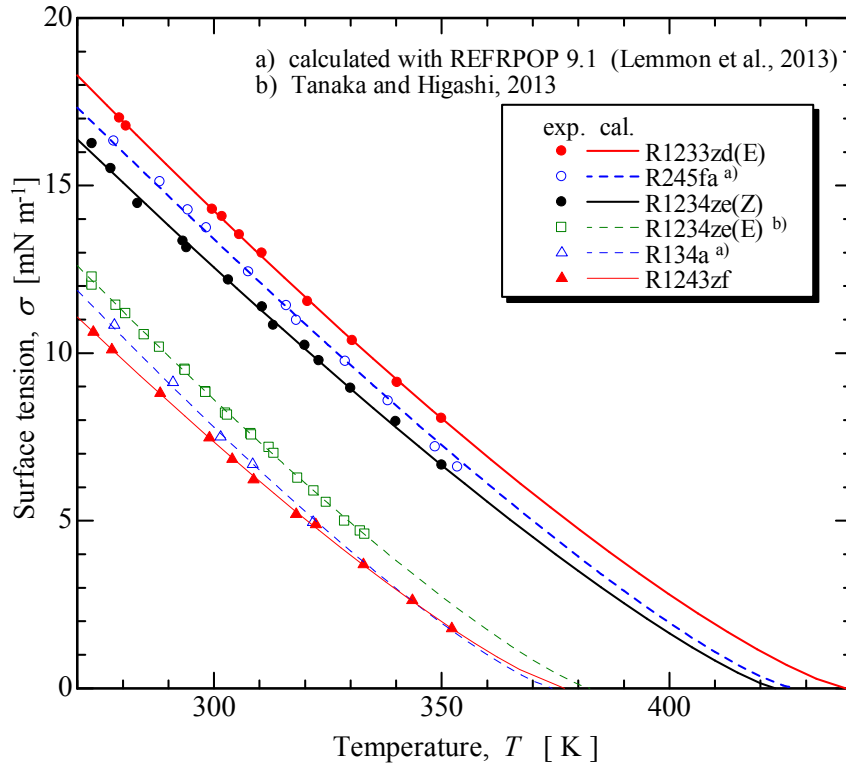


Figure 7 Comparison of surface tension between refrigerants

Table 1 Measurement uncertainties

measured parameter	equipment	uncertainty
temperature (ITS-90)	Platinum resistance thermometer and thermometer bridge, ASL F500	5 mK
differential capillary-rise-height, Δh_m	digital traveling microscope, Nippon optical works Co., Ltd., NRM-D-2XZ	0.046 mm (tolerance; 0.01 mm)
inner radii of the capillaries, r_1 and r_2	-	0.0009 mm
orthobaric densities, ρ' and ρ''	-	0.04% of the calculated values with the representative temperature

Table 2 Measured capillary constant and surface tension

	temperature (ITS-90)	liquid density	vapor density	capillary rise height difference	capillary constant	surface tension
	T	ρ^l	ρ^v	Δh_c	a^2	σ
	K	kg m ⁻³	kg m ⁻³	×10 ⁻³ m	×10 ⁻⁶ m ²	×10 ⁻³ N m ⁻¹
R1243zf						
series 1	298.97	975.62	27.55	1.67	1.72	7.47
	308.68	945.26	36.12	1.45	1.50	6.22
	318.04	913.85	46.50	1.27	1.33	5.19
series 2	303.99	960.18	31.73	1.56	1.61	6.84
	273.50	1047.34	12.65	2.18	2.20	10.63
	277.58	1036.50	14.45	2.10	2.12	10.10
	288.18	1007.24	20.09	1.89	1.93	8.80
	322.35	898.55	52.13	1.23	1.28	4.89
	332.81	858.60	68.61	0.99	1.06	3.70
	343.54	812.06	91.12	0.77	0.85	2.62
	352.22	768.10	115.70	0.58	0.66	1.78
R1234ze(Z)						
series 1	294.00	1231.44	7.67	2.28	2.19	13.15
	310.61	1187.64	13.09	2.06	1.98	11.38
	319.97	1161.56	17.29	1.90	1.83	10.23
	330.01	1132.27	22.96	1.71	1.65	8.95
	339.94	1101.73	30.01	1.58	1.52	7.96
	350.03	1068.67	38.	1.37	1.32	6.66
	273.22	1282.53	3.58	2.70	2.60	16.26
	277.34	1272.71	4.20	2.59	2.50	15.51
series 2	283.24	1258.37	5.24	2.45	2.46	14.47
	293.20	1233.48	7.46	2.31	2.33	13.35
	303.19	1207.58	10.38	2.16	2.18	12.19
	313.05	1180.96	14.09	1.97	2.00	10.83
	323.05	1152.75	18.89	1.83	1.87	9.78
R1233zd(E)						
series 1	299.64	1259.20	7.56	2.42	2.33	14.29
	310.54	1232.22	10.75	2.26	2.17	12.99
	320.56	1206.51	14.53	2.05	1.98	11.54
	330.37	1180.36	19.19	1.90	1.82	10.38
	340.23	1152.92	25.01	1.72	1.65	9.13
	349.98	1124.41	32.11	1.56	1.51	8.05
	305.58	1244.61	9.19	2.32	2.24	13.53
series 2	280.72	1303.97	3.82	2.74	2.64	16.78
	301.79	1253.94	8.12	2.40	2.31	14.08
	279.26	1307.32	3.61	2.77	2.67	17.02

Table 3 Fluid parameters used for the estimations, Eqs. (6) to (9)

			R1243zf	R1234ze(Z)	R1233zd(E)
critical temperature	T_{crit}	K	376.93 ^{c)}	423.27 ^{b)}	438.75 ^{a, e)}
critical pressure	P_{crit}	MPa	3.517 ^{c)}	3.533 ^{b)}	3.573 ^{a)}
normal boiling point	T_b	K	246.70 ^{c)}	283.40 ^{d)}	291.47 ^{a)}
acentric factor	ω	-	0.2605 ^{c)}	0.3274 ^{d)}	0.3050 ^{a)}
parachor ^{f)}	$[P]$	-	169.5	180.1	209.2

a) REFPROP 9.1 (Lemmon et al., 2013), b) Higashi *et al.* (2014), c) Akasaka (2015), d) Akasaka *et al.* (2014), e) Hulse *et al.* (2012), f) Reid *et al.* (1987)

Table 4 Assessment of the estimation methods

		Macleodo-Sugden (1923)	Miller (1963)	Miqueu <i>et al.</i> (2000)	Di Nicola <i>et al.</i> (2013)	Empirical correlation Eq. (13)
$\bar{\epsilon}$ [mN m ⁻¹] Eq. (10)	R1243zf	0.45	-0.05	0.09	-0.14	0.004
	R1234ze(Z)	0.70	-0.11	0.65	-0.37	-0.023
	R1233zd(E)	2.01	-0.35	-0.29	-0.54	-0.004
	overall	1.00	-0.16	0.19	-0.35	-0.009
$STDEV$ [mN m ⁻¹] Eq. (11)	R1243zf	0.16	0.09	0.08	0.06	0.055
	R1234ze(Z)	0.23	0.13	0.26	0.13	0.133
	R1233zd(E)	0.30	0.21	0.16	0.17	0.056
	overall	0.70	0.19	0.43	0.20	0.095