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# SURFACE TENSION MEASUREMENT OF LOW GWP REFRIGERANTS

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## ABSTRACT

HFOs (hydro-fluoro-olefins) are very recently under consideration as a potential candidate of R410A alternatives with GWP of 2800 that is most widely used in air-conditioning and refrigeration systems. The capillary constant and surface tension of R32, R1234ze(E), and their binary mixture R32/R1234ze(E) are measured in the temperature range from 274 K to 342 K by the differential capillary rise method. The propagated uncertainty in the surface tension is estimated within 0.3 mN m$^{-1}$. The experimentally quantified surface tensions of the components R32 and R1234ze(E) well agree with the calculated value by REFPROP 9.1. The measured surface tension of R32/R1234ze(E) at charged compositions 51/49 mass% and 43/57 mass% reasonably agree with the correlation for R32/R1234ze(E) (50/50 mass%) proposed by Tanaka and Higashi [1]. The surface tension data presented in this study and avairable in literatures (Tanaka and Higashi [1]; Cui et al. [2]) appear to vary almost linearly against mole fraction at a fixed reduced temperature.

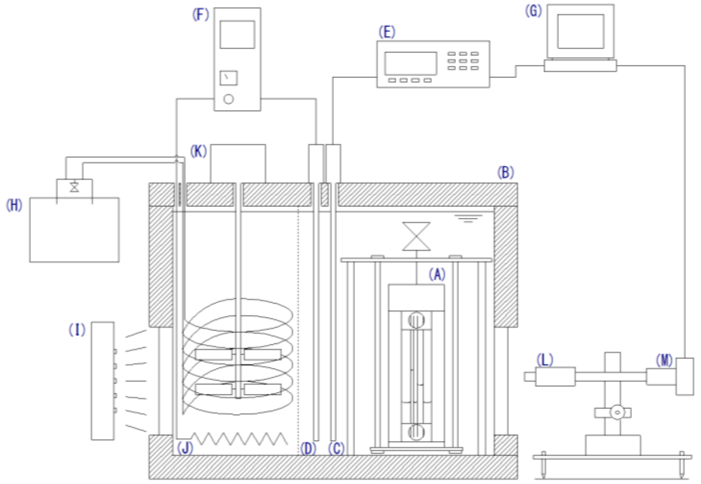
## 1. INTRODUCTION

In recent years, low GWP (global warming potential) refrigerants have been attracting the worldwide interest in air conditioning and refrigeration manufacturers. The current commercial focus is for R1234yf with a GWP of less than one (Myhre et al., [3]) to replace R134a in automotive applications. In addition to R1234yf, R1234ze(E) with a GWP of less than one is receiving commercial interest as a potential alternative refrigerant, blowing agent, and aerosol. However, because R1234ze(E) has smaller volumetric capacity than the conventional refrigerant R410A, using R1234ze(E) alone does not satisfy the same heating/cooling capacity, as R410A achieves (e.g., Mota-Babiloni, et al. [4]), without the drastic cycle modification or upsizing compressor, and so on. To maintain the rating heating/cooling capacity, increasing circulation ratio decreases the COP (coefficient of performance) due to the pressure loss. As the solution of this, adding R32 into R1234ze(E) was proposed by Fukuda et al. [5]. The surface tension is one of the most important parameter determines the heat transfer coefficient during boiling and condensation processes. Thus, surface tension data of R32/ R1234ze(E) are necessary for designing heat exchangers using this binary mixture. Tanaka and Higashi [1] reported the data of R32/R1234ze(E) (50/50 mass%) at temperatures across 273 K to 323 K measured by a capillary rise method. Later, Cui et al. [2] reported the data of mass fractions of 16.2/83.8 mass%, 37.6/62.4 mass%, and 57.8/42.2 mass%, measured by a surface light scattering. To updating the measurement data for the binary mixture, in this study, the measurement data by a capillary rise method are presented and compares with the data previously reported.

## 2. EXPERIMENTAL METHOD

### 2.1. Experimental apparatus

Fig. 1 shows an experimental apparatus designed for measuring the surface tension. This apparatus was originally develipped by Okada et al. [6] based on a capillary rise. 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 (Okada et al. [6]). 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 refrigerant is filled roughly to a half volume of the pressure vessels at a 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 ± 10 mK using a PID (F) controlled heater (J) and a chiller (H). The temperature is measured with a 100 Ω 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 a steady state, the capillary rise difference between the two capillary tubes is measured using a digital traveling microscope (L) with a tolerance of 0.01 mm.



(A) pressure vessel
(B) thermostatic bath
(C) platinum resistance thermometer (100 Ω)
(D) sheathed thermocouple
(E) thermometer bridge
(F) temperature control system (PID)
(G) computer
(H) chiller
(I) LED illumination
(J) electric heater
(K) stirrer
(L) traveling microscope
(M) CCD camera

Figure 1: Experimental apparatus.

## 2.2. Data reduction of differential capillary rise method

Fig. 2 illustrates the differential capillary-rise-height. Specifically, with the traveling microscope (L) and a CCD camera (M) shown in Fig.1, the height difference of the bottom of the meniscus in each capillary tubes, $\Delta h_m$ as shown in Fig. 2, is measured. Fig. 3 is the CCD image displayed on a monitor (G), shown in Fig. 1, to determine the position of the meniscus bottom. The differential height is read twice by different four persons (8 times reading in total) to avoid the individual reading variation. The two standard deviations of 8 times readings were 0.04 mm. This deviation is taken into account as the reading error in the differential height measurement. The contact angle $\theta$, shown in Fig. 2, is approximated as zero assuming the semispherical meniscus. To obtain the actual differential capillary rise height, the measured differential height $\Delta h_m$ at the bottom of the meniscus in each capillary tube is corrected by a methodology of Rayleigh [7].

$$\Delta h_c = \Delta h_m + \frac{r_1 - r_2}{3} - 0.1288\left(\frac{r_1^2}{h_{m1}} - \frac{r_2^2}{h_{m2}}\right) + 0.1312\left(\frac{r_1^3}{h_{m1}^2} - \frac{r_2^3}{h_{m2}^2}\right) + \ldots \approx \Delta h_m + \frac{(r_1 - r_2)}{3} \tag{1}$$

The capillary constant $a^2$ is determined only from the capillary radii, $r_1$ and $r_2$, and the differential capillary-rise-height, $\Delta h_c$.

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

where $g$ and $g_n$ are the local gravitational acceleration 9.79585 m s$^{-2}$ at Nagasaki-city, Japan and normal gravitational acceleration 9.80665 m s$^{-2}$, respectively. The contact angle $\theta$ of refrigerants in the capillary tube, which is well cleansed, is assumed zero. Hence the capillary constant is rewritten with the surface tension $\sigma$ as,

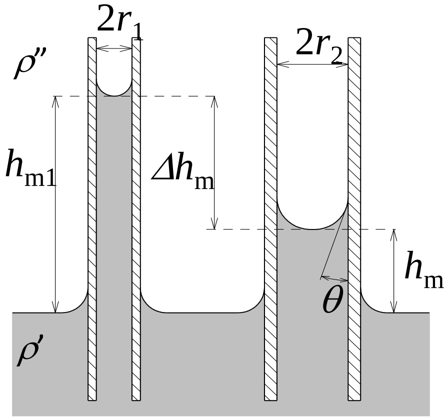


Figure 2: Principle of capillary rise method.

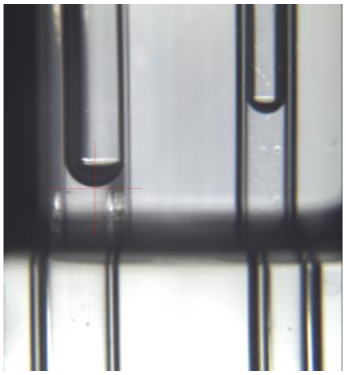


Figure 3: CCD image for the determination of bottom meniscus height.

$$a^2 = \frac{2\sigma}{g_n\left(\rho' - \rho''\right)} \tag{3}$$

where, $\rho'$ and $\rho''$ are the orthobaric liquid and vapour densities. Thus, the surface tension $\sigma$ is determined

$$\sigma = \frac{g\Delta h_c\left(\rho' - \rho''\right)}{2\left(1/r_1 - 1/r_2\right)\cos\theta} \approx \frac{g\Delta h_c\left(\rho' - \rho''\right)}{2\left(1/r_1 - 1/r_2\right)} \tag{4}$$

For the binary mixture R32/R1234ze(E), the following measurement procedure is introduced. The total charge amount, $m_{\mathrm{total}}$, and the composition, $\bar{X}$ , is determined from each mass of charged in the pressure vessel.

$$m_{\mathrm{total}} = m_{R32} + m_{\mathrm{R1234ze(E)}} \ , \tag{5}$$

$$\bar{X}_{\mathrm{R32}} = m_{\mathrm{R32}} / m_{\mathrm{total}} \tag{6}$$

The charge composition is checked with the completely vaporized sample in a large chamber by a TCD gas chromatograph The vapour quality in the vessel, $x$, is determined at a condition of satisfying the total volume is always equal to the internal volume of the pressure vessel.

$$V_{\mathrm{total}} = m_{\mathrm{total}} x / \rho_{\mathrm{V}}\left(\bar{X}, T, x\right) + m_{\mathrm{total}}\left(1 - x\right) / \rho_{\mathrm{L}}\left(\bar{X}, T, x\right) \tag{7}$$

The mass fractions of vapour and liquid phases can be calculated at that quality by REFPROP 9.1 (Lemmon et al. [8]). Accordingly, the vapor and liquid densities can be calculated as a function of charge composition, temperature, and quality. Substituting the above vapour and liquid densities, $\rho_{\mathrm{V}}$ and $\rho_{\mathrm{L}}$, into the orthobaric densities, $\rho'$ and $\rho''$, in Eq. (4), the surface tension is obtained for the binary mixture R32/R1234ze(E).

Figure 4 plots the surface tension measurement results of R134a and the deviation of the results from the calculated surface tension by REFPROP 9.1 [8] as a function of temperature. The various measurement data in literatures are also plotted for the comparison. The present data of series1 highly overlap to that of series 2, which are measured with the other sample re-charged. Those data agree with the calculated surface tension within ±0.2 mN m$^{-1}$, although the deviation shows a systematic characteristics: the slightly positive deviation at lower temperatures and the slightly negative deviation at higher temperatures. The measurement uncertainty (2k) is typically ±0.3 mN m$^{-1}$ that is greater than the deviation. Overall, the validation of repeatability and reproducibility is demonstrated with the most authorized value of R134a.

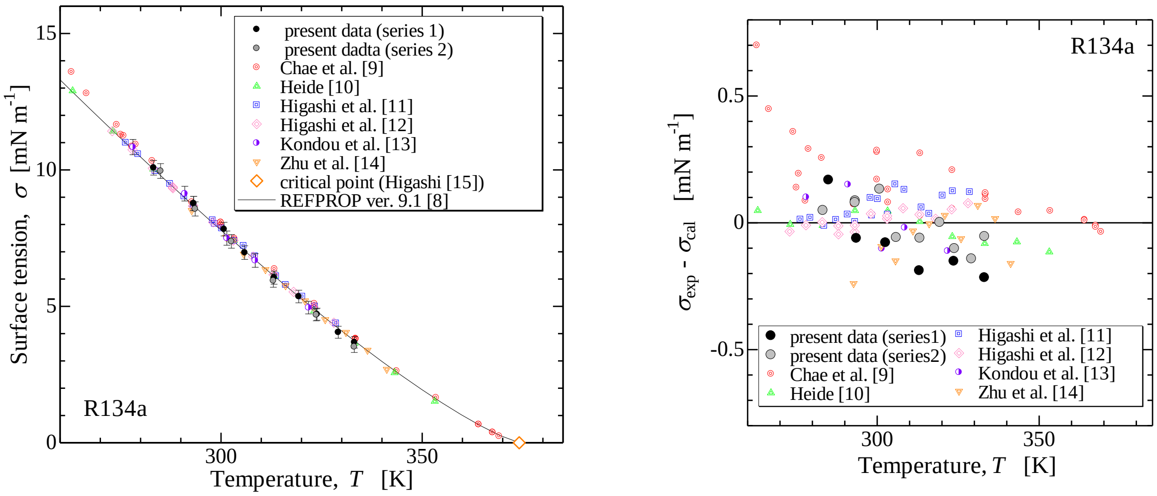


Figure 4: Surface tension of R134a

## 3. RESULTS AND DISCUSSION

### 3.1 Single components of R32 and R1234ze(E)

Figures 5 and 6 plot the present measured data for the component of R32 and R1234ze(E), respectively. The measurement data available in literatures and the calculated surface tension are also plotted. The measured data of R32 agree with the calculation within the deviation of ±0.012 mN m$^{-1}$ in the measurement range. On the other hand, the data of R1234ze(E) negatively deviated the calculation from 0 mN m$^{-1}$ to -0.5 mN m$^{-1}$. The deviation of R1234ze(E) is somewhat larger than the other results, probably because of the purification and the less data base. Nevertheless, the deviation is almost within the measurement uncertainty.

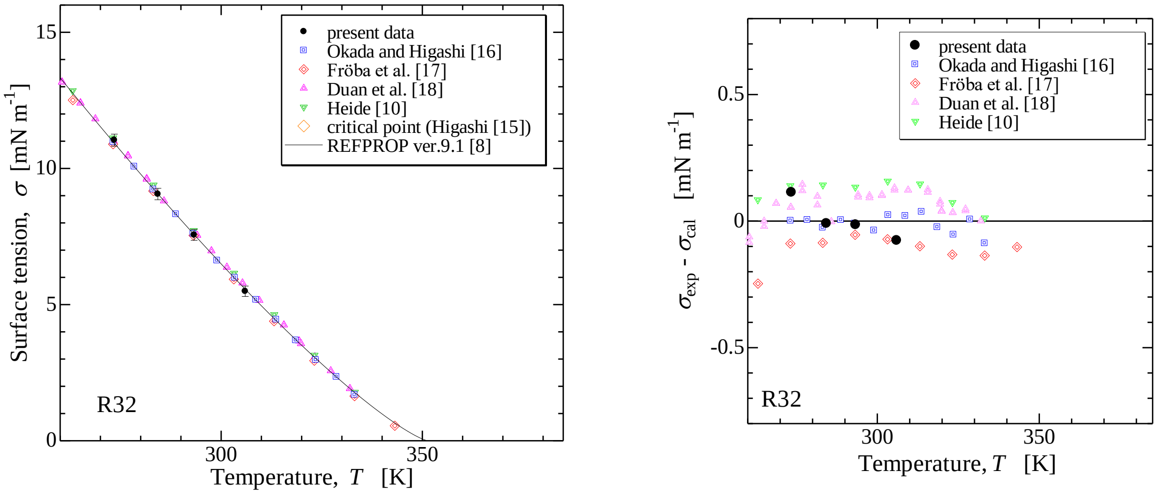


Figure 5: Surface tension of R32

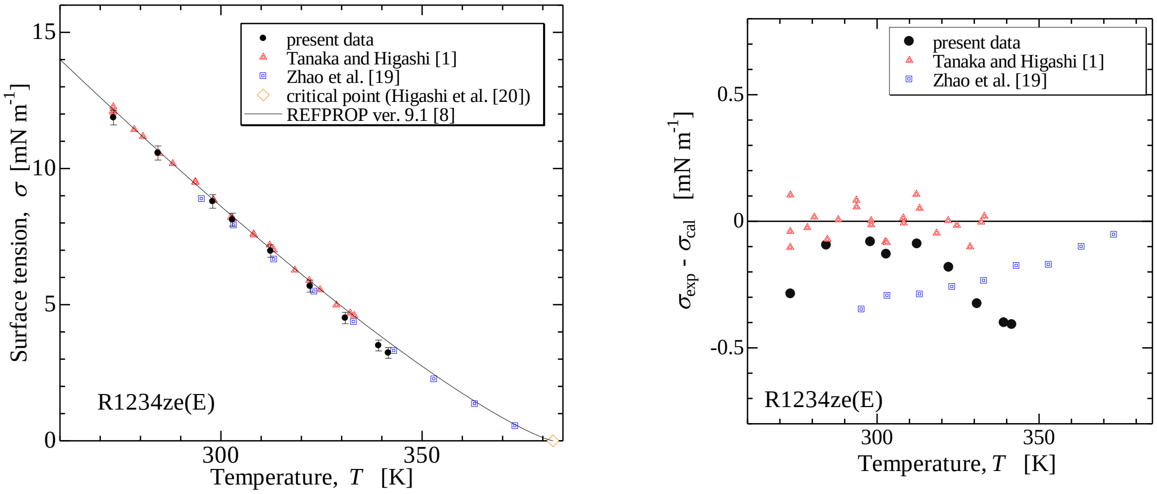


Figure 6: Surface tension of R1234ze(E)

### 3.2 Binary mixture of R32/R1234ze(E)

Figure 7 shows the measurement data for the binary mixture R32/R1234ze(E). The present data series 1 and 2 are measured at charged compositions 51/49 mass% and 43/57 mass%. In the series 1, the liquid mass fraction of R32 is estimated ranging from 0.48 to 0.50; meantime, the vapor mass fraction is estimated to be from 0.64 to 0.73. In the series 2, the liquid and vapor mass fraction of R32 are estimated to be from 0.40 to 0.42, and from 0.60 to 0.68, respectively. During the measurement of series 1 and series 2 vapor quality ranged from 0.03 to 0.16, which represented the range of void fraction from 0.65 to 0.80. Although, the composition is varied ±10 mass% around 50/50 mass%, the data of series 1 and 2 highly overlap.

In Figure 7, the red triangle and blue diamond show the data measured by Tanaka and Higashi [1] and by Cui et al. [2]. The composition of the data by Cui et al. [2], 58/52 mass%, slightly differs from the reference 50/50 mass%.

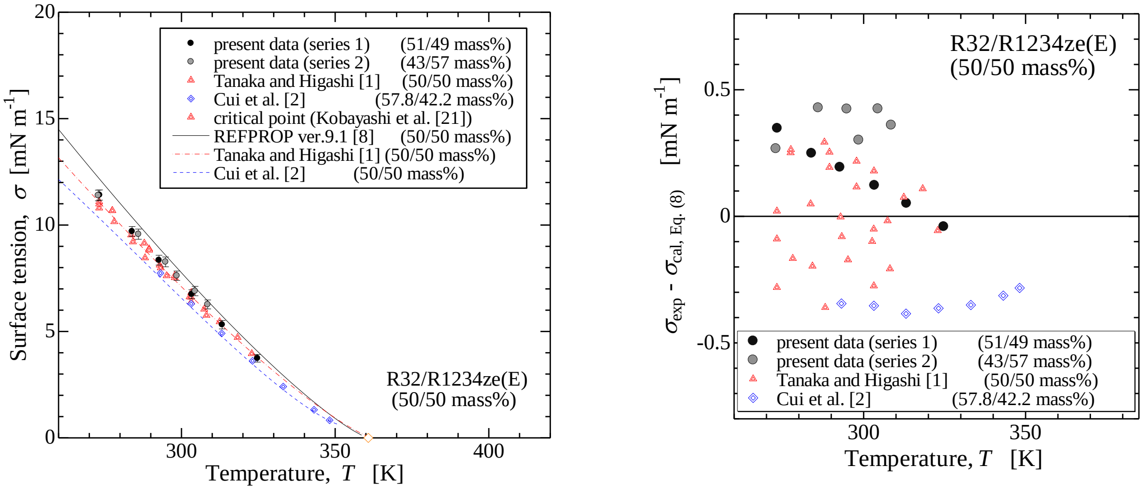


Figure 7: Surface tension of R32/R1234ze(E)

### 3.3 Effects of composition

The following correlations proposed by Tanaka and Higashi [1], and Cui et al. [2] are plotted with lines in Figure 7.

Tanaka and Higashi [1]: $\sigma_{\mathrm{R32/R1234ze(E)(50/50\ mass\%)}} = 63.37\left(1-\frac{T}{362.16}\right)^{1.242}$ (8)

The critical temperature of R32/R1234ze(E), $T_c = 362.16$ [K], reported by Kobayashi et al. [21] is introduced to the above calculation.

Cui et al. [2]: $\sigma_{\mathrm{R32/R1234ze(E)}} = \bar{X}_{\mathrm{R32}}\sigma_{\mathrm{R32}} + \bar{X}_{\mathrm{R1234ze(E)}}\sigma_{\mathrm{R1234ze(E)}} + \bar{X}_{\mathrm{R32}}\bar{X}_{\mathrm{R1234ze(E)}}\left(-6.6940+0.0207\cdot T\right)$ (9)

where, $\sigma_{\mathrm{R32}}$ and $\sigma_{\mathrm{R1234ze(E)}}$ are obtained from the correlations of Zhao et al. [19].

$$\begin{cases} \sigma_{\mathrm{R32}} = 48.813\left(1-\frac{T}{351.26}\right)^{1.26}\left[1+2.725\left(1-\frac{T}{351.26}\right)^{0.5}-3.884\left(1-\frac{T}{351.26}\right)\right] \\ \sigma_{\mathrm{R1234ze(E)}} = 57.905\left(1-\frac{T}{382.52}\right)^{1.26}\left[1-0.054\left(1-\frac{T}{382.52}\right)^{0.5}+0.064\left(1-\frac{T}{382.52}\right)\right] \end{cases} \qquad (10)$$

The present data show better fit to the correlation of Tanaka and Higashi at the measurement range. As compared in Figure 7, because of the slightly R32 richer composition, the data of Cui et al. [2] show the lower values. On the contrary, because of the slightly R1234ze(E) richer composition, the present data series 2, show the highest value.

To consider the effects of composition, the interpolated measurement data at a reduced temperature of 0.85, which corresponds temperatures from 299 K to 325 K, are plotted as a function of R32 mole fraction in Figure 8. In the same way, the data of the above two groups are also plotted. As shown in Figure 8, it appears to be that the surface tension at a reduced temperature of 0.85 varies almost linearly against the mole fraction.

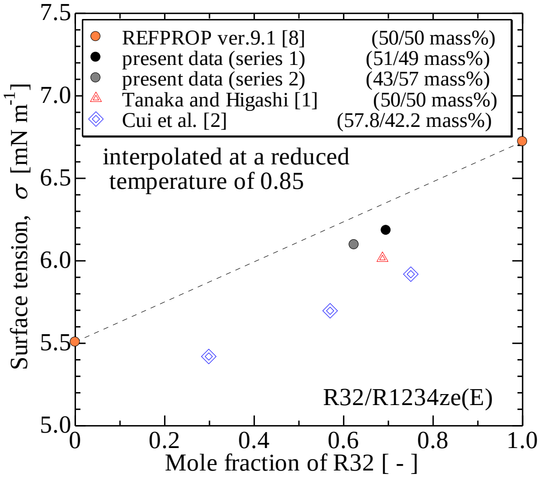


Figure 8: R32/R1234ze(E) surface tension variation against R32 mole fraction

## 4. CONCLUSIONS

The measurement data of surface tension by capillary rise method for binary mixture R32/R1234ze(E) are presented in this study. The measured surface tensions of R32 agree with the calculated one by REFPROP within ±0.012 mN m$^{-1}$ that is smaller than the measurement uncertainty. While that of R1234ze(E) deviates from the calculated value from 0 mN m$^{-1}$ to -0.5 mN m$^{-1}$. The surface tension of R32/R1234ze(E) is measured at charged compositions of 51/49 mass% and 43/57 mass%. The present data reasonably agreed with the correlation of Tanaka and Higashi [1]. The variation of present and previous data interpolated at a reduced temperature of 0.85 appear to be almost linear against the mole fraction.

## NOMENCLATURE

| | | | |
|---|---|---|---|
| $a^2$ | capillary constant (m$^2$) | $\overline{X}$ | charge mass fraction ( - ) |
| $g$ | local gravitational acccelration (m s$^{-2}$) | $\Delta h_c$ | corrected differential height (m) |
| $g_n$ | normal gravitational acceleration (m s$^{-2}$) | $\Delta h_m$ | measured differential height (m) |
| $m$ | mass (kg) | $\theta$ | contact angle (rad) |
| $r_1$ | smaller radius of capillary (m) | $\rho'$ | orthobaric vapour density (kg m$^{-3}$) |
| $r_2$ | larger radius of capillary (m) | $\rho''$ | orthobaric liquid density (kg m$^{-3}$) |
| $T$ | temperature (K) | $\rho_L$ | liquid density of mixture (kg m$^{-3}$) |
| $T_c$ | critical temperature (K) | $\rho_V$ | vapour density of mixture (kg m$^{-3}$) |
| $V$ | volume (m$^3$) | $\sigma$ | surface tension (N m$^{-1}$) |
| $x$ | vapour quality ( - ) | | |

Subscript

| | | | |
|---|---|---|---|
| R1234ze(E) | R1234ze(E) | R32/R1234ze(E) | R32/R1234ze(E) |
| R32 | R32 | Total | total |

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