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Surface Tension of HFC Refrigerant Mixtures[1]

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The surface tension of refrigerant mixtures, i.e., R-410A (50 mass% R-32/50 mass% R-125), R-410B (45 mass% R-32/55 mass% R-125), R-407C (23 mass% R-32/25 mass% R-125/52 mass% R-134a), R-404A (44 mass% R-125/52 mass% R-143a/4 mass% R-134a), and R-507 (50 mass% R-125/50 mass% R-143a), has been measured and correlated in the present study. Although the first three mixtures are very important as promising replacements for R-22 in air-conditioners and heat-pumps and the last two are promising replacements for R-502, surface tension data for these mixtures were not previously available. The measurements were conducted under conditions of coexistence of the sample liquid and its saturated vapor in equilibrium. The differential capillary rise method (DCRM) was used, with two glass capillaries with inner radii of 0.3034 ± 0.0002 and 0.5717 ± 0.0002 mm. The temperature range covered was from 273 to 323 K, and the uncertainty of measurements for surface tensions and temperatures is estimated to be at most $\pm 0.2\ \mathrm{mN \cdot m^{-1}}$ and ± 20 mK, respectively. A mixing rule was selected for representing the temperature dependence of the resultant data. These data were successfully represented by a mixing rule using mass fraction based on the van der Waals correlation.

KEY WORDS: differential capillary-rise method; mixtures; R-410A; R-410B; R-407C; R-404A; R-507; refrigerants; surface tension.

1. INTRODUCTION

As the phasing-out of hydrochlorofluorocarbons (HCFC) has started because of their ozone depletion potential, mixtures of hydrofluorocarbons

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(HFC) are some of the most promising alternatives to R-22 and R-502, which are the most widely used refrigerants at the present. Surface tension is a basic thermophysical property with respect to a vapor-liquid interface and is required to analyze the heat transfer during boiling and condensation in refrigeration and heat pump systems. This paper presents surface tension measurements for five refrigerant mixtures, i.e., R-410A (50 mass% R-32/50 mass% R-125), R-410B (45 mass% R-32/55 mass% R-125), R-407C (23 mass% R-32/25 mass% R-125/52 mass% R-134a), R-404A (44 mass% R-125/52 mass% R-143a/4 mass% R-134a), and R-507 (50 mass% R-125/50 mass% R-143a). The first three mixtures are very important as promising replacements for R-22 in air-conditioners and heat-pumps, and the last two are promising replacements for R-502. In addition, a mixing rule is discussed for representing the temperature dependence of the resultant data.

2. EXPERIMENTS

The experimental technique employed in obtaining surface tension data was based on the differential capillary-rise method, which is considered to be one of the most accurate methods. We have previously reported the measurements of surface tension for the alternative refrigerants for chlorofluorocarbons (CFC) by the differential capillary-rise method [1–3] and the same apparatus and procedure explained in those previous papers were also used in the present study.

In this method, two different capillaries with large and small radii r_1 and r_2 were used. The measured difference in the heights between the menisci in two capillaries was corrected for the amount of material above the meniscus. This was accomplished using Rayleigh's correction [4]. The surface tension σ was determined using the corrected difference in the heights $(h_1 - h_2)$ from the following relation.

$$\sigma = \frac{g(\rho' - \rho'')(h_1 - h_2)}{2(1/r_1 - 1/r_2)\cos\theta} \tag{1}$$

where θ denotes the contact angle of the liquid-vapor meniscus at the inner surface of capillary, g is the local acceleration of gravity (at Iwaki, Japan, $g = 9.8002\ \mathrm{m \cdot s^{-2}}$), and ρ' and ρ'' are the saturated vapor and liquid densities, respectively.

Two Pyrex glass capillaries were placed vertically in a pressure vessel composed of a thick-walled Pyrex glass tube (17 mm in inner diameter and 25 mm in outer diameter). The inner radii of two capillaries are 0.3034 ± 0.0002 and 0.5717 ± 0.0002 mm, respectively. These radii were determined by means of a mercury thread. The pressure vessel was installed in the thermostated bath. The temperature in the bath was maintained constant to within ±5 mK and measured based on ITS-90.

The difference in rise heights in the capillaries was determined by the measurement of the location of the meniscus in each capillary. The location of the bottom of the meniscus was measured through the window of the thermostated bath by a traveling microscope with an uncertainty of ±0.02 mm. The contact angle θ is assumed to be zero, since the inner walls of the capillaries were carefully washed and the capillary-rise height measurements were performed under the condition of a receding contact angle. The saturated liquid density values of R-410A and R-410B are calculated from the correlation by Widiatmo [5]. For other cases, the saturated vapor and liquid density values of mixtures are calculated from REFPROP Version 5.10 [6].

Asahi Glass Co. Ltd. furnished and analyzed the sample mixtures. The reported compositions are as follows.

R-410A: 49.6 mass% R-32/50.4 mass% R-125.
R-410B: 44.3 mass% R-32/55.7 mass% R-125.
R-407C: 22.5 mass% R-32/25.1 mass% R-125/52.4 mass% R-134a.
R-404A: 44.1 mass% R-125/51.8 mass% R-143a/4.1 mass% R-134a.
R-507: 49.9 mass% R-125/50.1 mass% R-143a.

As a precaution, the sample compositions of liquid phase were checked before and after the experiments using gas chromatography. The measured compositions agreed with the reported compositions within the experimental uncertainty of the measurements.

All of the measurements were carried out under equilibrium conditions between the liquid and its saturated vapor. The total uncertainty of the measurements for surface tensions and temperatures is estimated to be within $\pm 0.2\ \mathrm{mN \cdot m^{-1}}$ and ±20 mK, respectively.

3. RESULTS AND DISCUSSION

The experiment was repeated three times by refilling the cell with a fresh sample and repeating the measurements. This was done to verify the repeatability of the measurements. The experimental results that are listed in Table I are the mean value of repeated measurements at the same temperature. The capillary constant a^2 is also listed in Table I, as well as the surface tension, because it is not affected by the uncertainty of density

Table I. Experimental Results of the Surface Tension σ and Capillary Constant a^2 at Temperature T (ITS-90)

T (K)	a^2 (mm^2)	σ (mN·m^{-1})
	R-410A	
273.33	1.562	8.73
278.89	1.456	7.94
283.14	1.351	7.21
287.87	1.257	6.55
293.41	1.140	5.75
298.32	1.040	5.08
303.22	0.940	4.43
307.90	0.835	3.79
313.31	0.727	3.13
	R-410B	
273.33	1.523	8.62
278.53	1.397	7.71
283.27	1.309	7.09
288.10	1.206	6.34
293.32	1.101	5.62
298.18	1.016	4.96
303.18	0.901	4.30
308.15	0.804	3.68
312.86	0.704	3.08
	R-407C	
273.32	1.716	10.26
276.88	1.650	9.74
278.41	1.592	9.34
283.11	1.529	8.81
286.48	1.464	8.32
288.43	1.397	7.87
293.51	1.324	7.29
298.16	1.242	6.68
302.92	1.145	6.00
308.15	1.056	5.37
313.06	0.981	4.83
318.41	0.862	4.08
323.02	0.760	3.46

Table I. *(Continued)*

T (K)	a^2 (mm^2)	σ (mN$\cdot$m^{-1})
	R-404A	
273.33	1.395	7.64
278.27	1.285	6.88
283.27	1.224	6.40
287.83	1.137	5.80
293.28	1.012	5.00
298.23	0.949	4.53
303.21	0.817	3.76
308.28	0.750	3.31
	R-507	
273.32	1.343	7.39
278.24	1.234	6.64
283.31	1.181	6.19
288.27	1.069	5.45
293.25	0.981	4.85
298.26	0.887	4.24
303.09	0.811	3.74

values. The relation between the surface tension and the capillary constant is

$$a^2=\frac{(h_1-h_2)}{(1/r_1-1/r_2)\cos\theta}\cdot\frac{g}{g_n}=\frac{2\sigma}{g_n(\rho'-\rho'')} \tag{2}$$

where g_n denotes the normal acceleration of gravity of 9.80665 $\text{m}\cdot\text{s}^{-2}$.

The results in Table I show that the surface tension of mixtures decreases with increasing temperature and becomes zero at the critical point. This is the same behavior as observed for pure fluids. The following simple expression by van der Waals is known to represent the temperature dependence of the surface tension, σ, of pure fluids:

$$\sigma=\sigma_0(1-T/T_c)^n \tag{3}$$

where T and T_c denote the temperature (K) and the critical temperature (K), respectively. The σ_0 and n are numerical constants which depend on the substance. For mixtures, a similar expression was used:

$$\sigma_m=\sigma_{0m}(1-T/T_{cm})^{n_m} \tag{4}$$

where σ_{m} and T_{cm} denote the surface tension and the critical temperature (K) of the mixture, respectively. The $\sigma_{0\mathrm{m}}$ and n_{m} are numerical constants which are determined by a mixing rule. The following three types of mixing rules were tested:

$$\sigma_{0\mathrm{m}} = \sum_i \sigma_{0i} w_i; \qquad n_{\mathrm{m}} = \sum_i n_i w_i \tag{4a}$$

$$\sigma_{0\mathrm{m}} = \sum_i \sigma_{0i} x_i; \qquad n_{\mathrm{m}} = \sum_i n_i x_i \tag{4b}$$

$$\sigma_{0\mathrm{m}} = \sum_i \sigma_{0i} \theta_i; \qquad n_{\mathrm{m}} = \sum_i n_i \theta_i \tag{4c}$$

where σ_{0i} and n_i are the constants for component i. The values for the pure components were determined from the measured data in the previous work [2, 3]. The w_i denotes the mass fraction, x_i denotes the mole fraction, and θ_i denotes the surface fraction of each component i. The surface fraction, θ_i, is defined by the following relation,

$$\theta_i = \frac{x_i V_{ci}^{2/3}}{\sum_j x_j V_{cj}^{2/3}} \tag{5}$$

where V_{ci} and V_{cj} denote the critical molar volume of components i and j. These three types of mixing rule were compared using the present results. The results showed that Eq. (4a), which uses the mass fraction, produced the best agreement between the fit and the data for every mixture. Therefore, the coefficients, σ_0, $\sigma_{0\mathrm{m}}$, n, and n_{m} used in Eq. (4a), the cited critical temperatures T_{c} and T_{cm} and the literature sources [7–12] for these substances are listed in Table II.

Table II. Numerical Constants in Eqs. (3) and (4a)

Refrigerant	σ_{0i} or $\sigma_{0\mathrm{m}}$ $(\mathrm{mN \cdot m^{-1}})$	n_i or n_{m}	T_{ci} or T_{cm} (K)
R-32	72.16 [2]	1.252 [2]	351.26 [7]
R-125	52.60 [2]	1.240 [2]	339.17 [7]
R-134a	55.81 [3]	1.213 [3]	374.11 [7]
R-143a	54.27 [3]	1.259 [3]	345.88 [8]
R-410A	62.38	1.246	344.56 [9]
R-410B	61.40	1.245	343.89 [9]
R-407C	58.77	1.229	359.23 [10]
R-404A	53.60	1.249	345.18 [11]
R-507	53.44	1.250	343.76 [12]

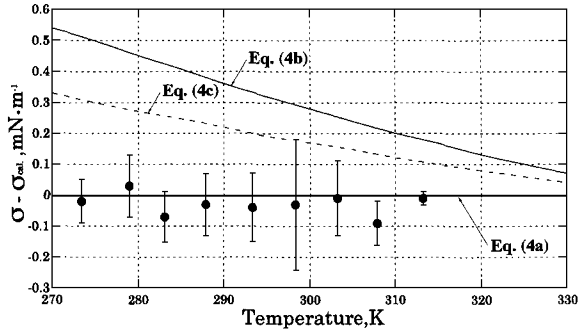

Fig. 1. Deviations of the surface tension of R-410A from Eq. (4a). Filled dots represent measured data, the solid line represents Eq. (4b), and the dashed line represents Eq. (4c).

The deviation plots from Eq. (4a) for five mixtures are illustrated in Figs. 1–5. In these figures, each symbol shows the present experimental result and the error bar shows the standard deviation of repeated measurements. The error bar shows that the repeatability is within the estimated uncertainty of ± 0.2 mN $\cdot$ m^{-1} in most cases. Experimental data of other investigators are not available and, thus, are not plotted on these figures. The deviation plots also show that Eq. (4a) represents most of the experimental surface-tension data for these five mixtures within experimental uncertainty. This means the mixing rule by mass fraction is most appropriate for these mixtures.

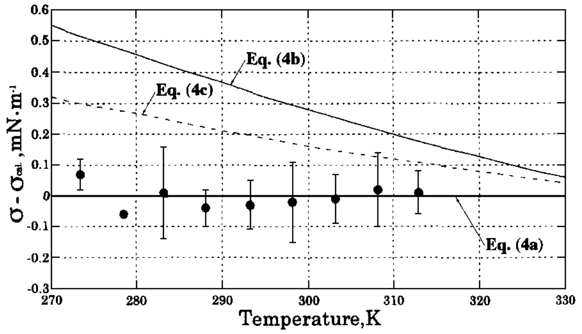

Fig. 2. Deviations of the surface tension of R-410B from Eq. (4a). Filled dots represent measured data, the solid line represents Eq. (4b), and the dashed line represents Eq. (4c).

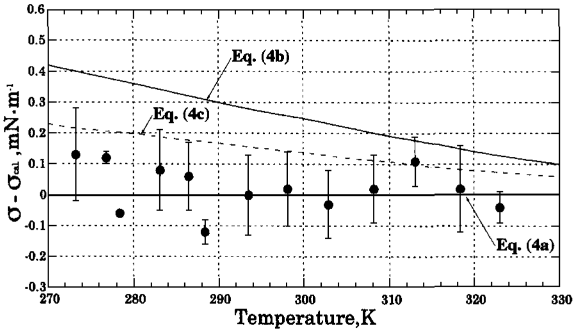

Fig. 3. Deviations of the surface tension of R-407C from Eq. (4a). Filled dots represent measured data, the solid line represents Eq. (4b), and the dashed line represents Eq. (4c).

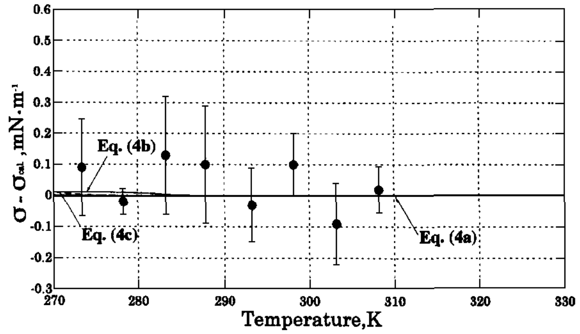

Fig. 4. Deviations of the surface tension of R-404A from Eq. (4a). Filled dots represent measured data, the solid line represents Eq. (4b), and the dashed line represents Eq. (4c).

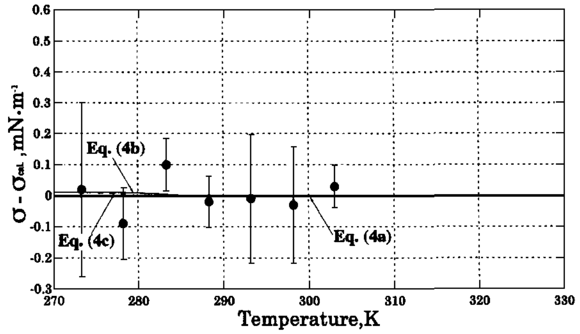

Fig. 5. Deviations of the surface tension of R-507 from Eq. (4a). Filled dots represent measured data, the solid line represents Eq. (4b), and the dashed line represents Eq. (4c).

4. CONCLUSION

The surface tensions of five refrigerant mixtures were measured over a wide temperature range using the differential capillary-rise method. The experimental results of this study are accurately represented by the van der Waals expression based on the mixing rule by mass fraction.

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