372 *J. Chem. Eng. Data* **2004,** *49,* 372−375

Surface Tension for the 1,1,1-Trifluoroethane (R-143a) + 1,1,1,2-Tetrafluoroethane (R-134a) System

Hong Lin and Yuan-Yuan Duan*

Department of Thermal Engineering, Tsinghua University, Beijing, 100084, China

The surface tensions of the binary mixtures 1,1,1-trifluoroethane (R-143a) + 1,1,1,2-tetrafluoroethane (R-134a) were measured in the temperature range from (257 to 329) K using the differential capillary rise method under vapor−liquid equilibrium conditions. The uncertainties of measurements for the temperature and surface tension were estimated to be within ±10 mK and ±0.15 mN·m^{-1}, respectively. The experimental surface tension data of R-143a + R134a were correlated as a function of the mass fraction using the correlations for pure R-143a and R-134a.

Introduction

Current knowledge indicates that only refrigerant mixtures are to be considered as alternatives to the ozone-damaging refrigerants chlorodifluoromethane (R-22) and R-502, whereby the mixture components must be substances with no ozone depletion potential (ODP = 0). Hydrofluorocarbon (HFC) mixtures are expected to be promising interim and long-term alternatives. The thermophysical properties of the mixtures are needed in order to set up models to evaluate the economic and technical effectiveness of the refrigeration systems in which these refrigerants are used. Surface tension is a basic thermophysical property with respect to the liquid−vapor interface and is actually quantified to analyze the heat transfer through heat-exchanging surfaces with bubbles or fluid drops.

In this paper, surface tension data of the binary mixture 1,1,1-trifluoroethane (R-143a) + 1,1,1,2-tetrafluoroethane (R-134a) were obtained at three nominal mass fractions (the liquid and vapor average composition) in the temperature range from (257 to 329) K and correlated as a function of the mass fraction using the correlations of pure R-143a and R-134a.

Experimental Section

Chemicals. The sample of pure R-143a was purchased from Zhejiang Fluoro-Chemical Technology Research Institute and used without further purification. The manufacturer stated that the purity was more than 99.95 mass %. R-134a was obtained commercially from Honeywell and used without further purification. The sample purity stated by the manufacturer was more than 99.95 mass %. Before use, the samples of R-143a and R-134a in sample bottles were frozen by liquefied nitrogen and the vapor space was evacuated by a vacuum pump (KYKY FD110) to remove possible air impurity. The samples were examined by a gas chromatograph (Lunan SP-6800A, an ODPN column) with a thermal conductivity detector (TCD), and no impurities were detected.

Apparatus and Procedure. The surface tension was measured using a direct optical measurement system. The apparatus and the procedure have been described in detail in previous work$^{1-3}$ and are only briefly described here.

The sample cell contains three capillaries with inner radii of $r_1 = (0.390 \pm 0.001)$ mm, $r_2 = (0.259 \pm 0.001)$ mm, and $r_3 = (0.125 \pm 0.001)$ mm. The three capillary radii were determined by partially filling the capillaries with mercury slugs of different masses. The temperature-measurement system includes platinum resistance thermometers (Tinsley, 5187SA) with an uncertainty of ±2 mK, a precision thermometer bridge (Tinsley, 5840D) with an accuracy within ±1 mK, a select switch (Tinsley, 5840CS/6T), and a personal computer. The temperatures were determined on the international temperature scale of 1990 (ITS-90). All of the temperature-measurement equipment was calibrated by the NIM (National Institute of Metrology, China) before the experiments in 2003. The overall temperature uncertainty including the bath instability and the temperature-measurement system was less than ±10 mK. The differences between the capillary rise heights were determined by measuring the meniscus locations in each capillary through a transparent window of the sample cell using a traveling telescope with an uncertainty of ±10 μm.

The mass of each component introduced into the sample cell was determined with an accurate electronic balance (Mettler Toledo PR1203) with a resolution of ±0.001 g. Three R-143a (1) + R-134a (2) binary mixtures were prepared at nominal mass fractions w_1' of 0.2688, 0.5714, and 0.7576. The binary mixture of R-143a + R-134a in the sample cell was prepared by placing the required masses of R-143a and R-134a in separate gas cylinders. The two cylinders were precisely weighed on the accurate electronic balance. The sample cell and connections were then evacuated by a vacuum pump (KYKY FD110) to remove impurities. The system vacuum was <10^{-4} Pa and was maintained for at least 5 h. A target amount of R-134a was introduced into the sample cell from the gas cylinder, and then the valve to the sample cell was closed and the cylinder was cooled by liquefied nitrogen to force the vapor in the pipeline to flow back to the gas cylinder. After the sample cell was cooled by the liquefied nitrogen, the required mass of R-143a was added to the sample cell from the other gas cylinder using the same procedure as

---

* Corresponding author. Telephone: +86-10-6278-2484. Fax: +86-10-6277-0209. E-mail: yyduan@te.tsinghua.edu.cn.

10.1021/je0342163 CCC: $27.50

Table 1. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' =$ 0.2688 for R-143a (1) + R-134a (2) with Liquid Mass Fraction w_1

				a^2/mm^2		σ/mN·m^{-1}	
T/K	ρ_l/kg·m^{-3}	ρ_v/kg·m^{-3}	w_1	(3,2)	(3,1)	(3,2)	(3,1)
257.03	1265	10.6	0.2630	2.050	2.050	12.60	12.60
258.87	1260	11.4	0.2627	2.027	2.023	12.40	12.38
264.97	1241	14.1	0.2618	1.906	1.906	11.46	11.46
268.83	1229	16.1	0.2611	1.840	1.841	10.94	10.94
271.15	1221	17.4	0.2607	1.800	1.801	10.62	10.62
273.20	1215	18.6	0.2604	1.772	1.772	10.39	10.39
275.43	1207	20.0	0.2600	1.732	1.728	10.07	10.05
277.04	1202	21.0	0.2597	1.699	1.704	9.83	9.86
279.15	1195	22.5	0.2593	1.653	1.653	9.50	9.50
281.43	1187	24.1	0.2589	1.620	1.620	9.23	9.23
282.89	1182	25.2	0.2586	1.590	1.589	9.01	9.01
285.24	1174	27.1	0.2581	1.547	1.548	8.69	8.70
287.40	1166	28.9	0.2577	1.503	1.518	8.37	8.46
289.31	1160	30.6	0.2573	1.488	1.488	8.23	8.23
291.37	1152	32.6	0.2569	1.463	1.463	8.03	8.03
293.21	1145	34.4	0.2565	1.416	1.423	7.71	7.74
293.45	1145	34.6	0.2564	1.388	1.395	7.55	7.59
295.58	1137	36.8	0.2560	1.351	1.353	7.28	7.29
297.38	1130	38.8	0.2556	1.320	1.320	7.06	7.06
299.53	1122	41.3	0.2552	1.299	1.289	6.88	6.83
301.53	1114	43.7	0.2547	1.258	1.253	6.60	6.57
303.66	1106	46.4	0.2542	1.221	1.216	6.34	6.31
305.56	1098	48.9	0.2538	1.191	1.194	6.12	6.14
307.46	1090	51.6	0.2534	1.146	1.148	5.83	5.84
309.60	1081	54.8	0.2529	1.113	1.108	5.60	5.57
311.25	1075	57.3	0.2525	1.082	1.077	5.40	5.37
313.55	1065	61.1	0.2520	1.039	1.033	5.11	5.08
315.59	1056	64.6	0.2515	1.000	0.996	4.86	4.84
317.36	1048	67.8	0.2511	0.973	0.967	4.67	4.65
319.66	1037	72.2	0.2506	0.935	0.930	4.42	4.40
322.01	1026	77.0	0.2500	0.888	0.883	4.13	4.11
323.26	1020	79.7	0.2497	0.870	0.865	4.01	3.99
325.69	1008	85.1	0.2492	0.811	0.811	3.67	3.67
327.33	999.7	89.1	0.2488	0.793	0.796	3.54	3.55

that for R-134a. The mass differences between the gas cylinders before and after the charging process were taken as the mass of each refrigerant in the sample cell and were used to calculate the nominal mass fractions in the sample cell. Since the sample mass to fill the sample cell was about 100 g, the mixture nominal mass fraction uncertainty was estimated to be better than ±0.01%.

The sample cell was a cylinder having a volume of 0.353 L at room temperature, as determined by carefully filling with distilled water. The R-143a (1) + R-134a (2) mixtures at the three nominal mass fractions w_1' of 0.2688, 0.5714, and 0.7576 are zeotropic blends, so the coexisting liquid and vapor compositions differed. The mass fractions of liquid and vapor phases were calculated using the sample cell volume, the sample masses in the cell, and the densities of the saturated liquid and vapor. The saturated liquid and vapor densities were obtained from NIST REFPROP 6.01.[4] The liquid height in the sample cell was also measured to check the precision of the calculation. To verify the results, the gas phase composition was checked using the gas chromatograph after the surface tension measurements. The detector response was carefully calibrated using gravimetrically prepared mixtures. The differences between the measured compositions and the calculated compositions are within ±0.2%.

All of the measurements were carried out under equilibrium conditions between the liquid and its saturated vapor. The total error analysis gave the estimated surface tension and temperature measurement accuracies to be within ±0.15 mN·m^{-1} and ±10 mK, respectively.

Table 2. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' =$ 0.5714 for R-143a (1) + R-134a (2) with Liquid Mass Fraction w_1

				a^2/mm^2		σ/mN·m^{-1}	
T/K	ρ_l/kg·m^{-3}	ρ_v/kg·m^{-3}	w_1	(3,2)	(3,1)	(3,2)	(3,1)
257.14	1182	13.2	0.5656	2.011	2.002	11.52	11.47
260.95	1170	15.1	0.5650	1.915	1.921	10.84	10.87
263.05	1164	16.2	0.5646	1.863	1.866	10.48	10.50
265.07	1157	17.3	0.5643	1.861	1.862	10.39	10.40
266.84	1152	18.4	0.5640	1.803	1.805	10.02	10.03
268.92	1145	19.7	0.5636	1.784	1.774	9.84	9.78
270.52	1140	20.7	0.5633	1.725	1.725	9.46	9.46
273.07	1132	22.5	0.5628	1.683	1.680	9.15	9.13
274.99	1125	23.9	0.5625	1.634	1.636	8.82	8.83
277.27	1118	25.6	0.5620	1.601	1.602	8.57	8.58
278.99	1112	27.0	0.5617	1.570	1.571	8.35	8.35
281.48	1103	29.2	0.5612	1.520	1.520	8.00	8.00
283.35	1097	30.8	0.5608	1.483	1.485	7.75	7.76
285.20	1090	32.6	0.5604	1.440	1.441	7.46	7.47
287.35	1082	34.7	0.5599	1.422	1.421	7.30	7.29
289.29	1075	36.8	0.5595	1.403	1.393	7.14	7.09
291.20	1068	38.9	0.5591	1.345	1.360	6.78	6.86
293.49	1060	41.5	0.5585	1.306	1.287	6.52	6.42
295.16	1054	43.6	0.5582	1.233	1.243	6.11	6.15
297.52	1044	46.6	0.5576	1.205	1.199	5.89	5.86
299.51	1037	49.3	0.5571	1.185	1.178	5.74	5.70
302.95	1023	54.3	0.5563	1.127	1.121	5.35	5.32
305.21	1013	57.8	0.5557	1.075	1.085	5.03	5.08
307.40	1004	61.4	0.5552	1.032	1.027	4.77	4.74
309.30	995.8	64.8	0.5547	1.004	0.996	4.58	4.54
311.41	986.5	68.6	0.5541	0.952	0.957	4.28	4.30
313.61	976.4	72.9	0.5536	0.905	0.914	4.01	4.05
315.30	968.6	76.4	0.5531	0.871	0.879	3.81	3.84
317.41	958.5	81.0	0.5525	0.832	0.845	3.58	3.63
319.33	949.1	85.5	0.5520	0.806	0.807	3.41	3.42
321.33	938.9	90.3	0.5515	0.763	0.766	3.17	3.19
323.42	928.0	95.8	0.5509	0.712	0.724	2.90	2.95
325.17	918.6	100.6	0.5505	0.685	0.687	2.75	2.75
327.38	906.3	107.1	0.5498	0.644	0.648	2.52	2.54
329.44	894.4	113.6	0.5493	0.607	0.606	2.32	2.32

Results and Discussion

The height h_0 of the bottom of the meniscus in each capillary was measured, and the actual rise height h was calculated using the following Rayleigh correlation:[5]

$$h = h_0 + r/3 - 0.1288r^2/h_0 + 0.1312r^3/h_0^{\,2} \tag{1}$$

where r is the radius of a capillary. The capillary constant a^2 can be related to the difference in the heights ($h_1 - h_2$) as

$$a^2 = \frac{h_1 - h_2}{(1/r_1) - (1/r_2)} \tag{2}$$

The surface tension can be calculated using the following expression as

$$\sigma = \frac{(\rho_l - \rho_v)g}{2}a^2 = \frac{(\rho_l - \rho_v)g}{2}\,\frac{(h_1 - h_2)}{[(1/r_1) - (1/r_2)]} \tag{3}$$

where σ is the surface tension, g is the local gravitational acceleration (at Beijing China g = 9.8015 m·s^{-2}), and ρ_l and ρ_v are the densities of the saturated liquid and vapor, respectively. ρ_l and ρ_v were calculated using NIST REFPROP 6.01[4] for the refrigerant mixture R-143a + R-134a. Two sets of surface tension results were obtained using the height difference between capillaries 3 and 2 and between capillaries 3 and 1. The results are listed in Tables 1−3, as well as the saturated liquid density ρ_l, the saturated vapor density ρ_v, the capillary constant a^2, and the liquid

Table 3. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' = 0.7576$ for R-143a (1) + R-134a (2) with Liquid Mass Fraction w_1

				a^2/mm^2		σ/mN·m^{-1}	
T/K	ρ_l/kg·m^{-3}	ρ_v/kg·m^{-3}	w_1	(3,2)	(3,1)	(3,2)	(3,1)
256.91	1136	14.4	0.7511	1.940	1.949	10.66	10.71
258.79	1130	15.4	0.7508	1.890	1.908	10.32	10.42
261.00	1123	16.6	0.7503	1.868	1.868	10.13	10.13
262.96	1117	17.8	0.7500	1.817	1.821	9.79	9.81
264.97	1111	19.0	0.7496	1.796	1.797	9.61	9.62
267.09	1104	20.3	0.7491	1.737	1.745	9.22	9.27
268.62	1099	21.4	0.7488	1.734	1.739	9.16	9.18
270.60	1093	22.8	0.7484	1.684	1.687	8.83	8.85
273.23	1084	24.7	0.7478	1.632	1.639	8.47	8.51
275.40	1077	26.5	0.7473	1.603	1.607	8.25	8.27
279.35	1064	29.9	0.7463	1.528	1.534	7.74	7.77
281.54	1056	31.9	0.7458	1.487	1.486	7.46	7.46
283.39	1050	33.7	0.7453	1.456	1.456	7.25	7.25
285.45	1042	35.9	0.7448	1.416	1.417	6.98	6.99
287.39	1035	38.0	0.7443	1.376	1.377	6.72	6.73
289.05	1029	39.9	0.7438	1.340	1.341	6.50	6.50
291.17	1021	42.4	0.7432	1.300	1.300	6.23	6.23
293.71	1012	45.6	0.7425	1.228	1.229	5.82	5.82
295.56	1005	48.1	0.7419	1.191	1.190	5.58	5.58
297.49	996.9	50.8	0.7413	1.161	1.158	5.38	5.37
299.41	989.2	53.7	0.7407	1.117	1.125	5.12	5.16
301.41	981.0	56.8	0.7401	1.075	1.084	4.87	4.91
303.65	971.6	60.5	0.7394	1.040	1.035	4.64	4.62
305.38	964.3	63.5	0.7388	1.006	0.998	4.44	4.41
307.74	953.9	67.8	0.7380	0.962	0.958	4.18	4.16
309.65	945.4	71.5	0.7373	0.926	0.926	3.97	3.97
311.44	937.1	75.2	0.7367	0.887	0.889	3.75	3.76
313.47	927.5	79.6	0.7360	0.838	0.848	3.48	3.52
315.54	917.5	84.3	0.7352	0.808	0.808	3.30	3.30
317.57	907.3	89.3	0.7345	0.771	0.780	3.09	3.13
319.39	897.9	94.0	0.7338	0.729	0.730	2.87	2.88
321.23	888.1	99.1	0.7331	0.690	0.699	2.67	2.70
323.33	876.6	105.2	0.7323	0.641	0.652	2.42	2.46
325.28	865.4	111.4	0.7315	0.605	0.612	2.24	2.26
327.36	853.1	118.4	0.7306	0.575	0.573	2.07	2.06
329.42	840.2	125.9	0.7298	0.514	0.521	1.80	1.82

Table 4. Numerical Constants in Equation 4 for R-143a and R-134a

refrigerants	σ_0/mN·m^{-1}	n	T_c/K
R-143a	53.7124 (ref 3)	1.245 (ref 3)	345.86 (ref 7)
R-134a	60.74 (ref 8)	1.262 (ref 8)	374.21 (ref 8)

Table 5. Coefficient in Equation 5 and Absolute and Relative Deviations between Experimental and Calculated Values

mixture	C/mN·m^{-1}	$\overline{\delta_a}^a$/mN·m^{-1}	$\overline{\delta_r}^a$/%
R-143a + R-134a	−1.0279	0.046	0.73

$^a\overline{\delta_a} = \frac{1}{n}\sum_{i=1}^{n}|\sigma_{\mathrm{exp},i} - \sigma_{\mathrm{cal},i}|$; $\overline{\delta_r} = \frac{1}{n}\sum_{i=1}^{n}\frac{|\sigma_{\mathrm{exp},i} - \sigma_{\mathrm{cal},i}|}{\sigma_{\mathrm{cal},i}}$

mass fraction of R-143a (w_1) in the mixtures at each temperature.

The surface tension of pure fluids is usually correlated as the following simple van der Waals type expression:

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n \tag{4}$$

where σ_0 and n are empirical constants obtained from a least-squares fit of the experimental data. T and T_c are the temperature and the critical temperature, respectively. Based on the correlation of pure fluids, the surface tension of binary refrigerant mixtures can be represented as[6]

$$\sigma = w_1\sigma_1 + w_2\sigma_2 + w_1 w_2 C \tag{5}$$

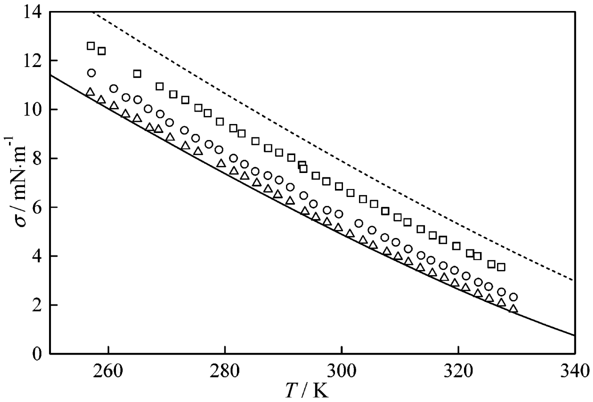

Figure 1. Surface tension vs temperature of R-143a (1) + R-134a (2): □, $w_1' = 0.2688$; ○, $w_1' = 0.5714$; △, $w_1' = 0.7576$; —, R-143a (ref 3); - - -, HFC-134a (ref 8).

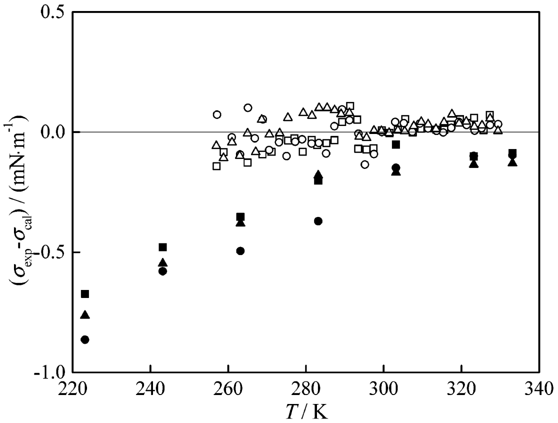

Figure 2. Absolute deviations of experimental surface tension data of R-143a (1) + R-134a (2) from eq 5: □, $w_1' = 0.2688$; ○, $w_1' = 0.5714$; △, $w_1' = 0.7576$; ■, $w_1' = 0.715$, Heide (ref 6); ●, $w_1' = 0.479$, Heide (ref 6); ▲, $w_1' = 0.230$, Heide (ref 6).

where σ_1 and σ_2 are the surface tension of the pure refrigerants calculated using eq 4 and w_1 and w_2 are the liquid mass fractions. The coefficient C was determined by fitting eq 5 to the present experimental data. Table 4 lists the coefficients σ_0 and n for pure R-143a and R-134a, also including the critical temperature. Table 5 lists the values of C, the average absolute deviation, and the average relative deviation of the present experimental data from eq 5.

Figure 1 shows the surface tension variation for the R-143a + R-134a mixtures and pure R-143a and pure R-134a as a function of temperature. The absolute deviation plots from eq 5 for R-143a + R-134a mixtures with various mass fractions are illustrated in Figure 2. The results in Figure 2 show that the absolute deviations of the present data from eq 5 are less than ±0.15 mN·m^{-1}. Heide's measurements[6] agree well with our results for temperatures above 280 K but are (0.4 to 0.9) mN·m^{-1} lower than the values from eq 5 for the temperature range from (220 to 280) K.

Conclusions

The surface tensions of R-143a + R-134a mixtures were measured over a wide temperature range using the differential capillary rise method at three nominal mass fractions. The present experimental results were then used to develop a correlation for the surface tension of the binary mixture R-143a + R-134a. The available literature data were compared with the correlation.

Literature Cited

(1) Zhu, M. S.; Han, L. Z.; Lu, C. X. Surface Tension of HFC-134a. *Fluid Phase Equilib.* **1993**, *86*, 363−367.

(2) Duan, Y. Y.; Lin, H.; Wang, Z. W. Surface Tension Measurements of Difluoromethane (R-32) and the Binary Mixture Difluoromethane (R-32) + 1,1,1,2-Tetrafluoroethane (R-134a) from (253 to 333) K. *J. Chem. Eng. Data* **2003**, *48*, 1068−1072.

(3) Lin, H.; Duan, Y. Y. Surface Tension of 1,1,1-Trifluoroethane (HFC-143a), 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea), and Their Binary Mixture HFC-143a/227ea. *Int. J. Thermophys.* **2003**, *24*, 1495−1508.

(4) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. W. *NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures (REFPROP)*, version 6.01; National Institute of Standards and Technology: Gaithersburg, MD, 1998.

(5) Rayleigh, O. M. On the Theory of Capillary Tube. *Proc. R. Soc. London, Ser. A* **1916**, *92*, 184−195.

(6) Heide, R. The Surface Tension of HFC Refrigerants and Mixtures. *Int. J. Refrig.* **1997**, *20*, 496−503.

(7) Aoyama, H.; Kishizawa, G.; Sato, H.; Watanabe, K. Vapor−Liquid Coexistence Curve in the Critical Region and the Critical Temperatures and Densities of 1,1,1,2-Tetrafluoroethane (R-134a), 1,1,1-Trifluoroethane (R-143a), and 1,1,1,2,3,3-Hexafluoropropane (R-236ea). *J. Chem. Eng. Data* **1996**, *41*, 1046−1051.

(8) Duan, Y. Y.; Zhang, C. H.; Shi, L.; Zhu, M. S.; Han, L. Z. Surface Tension Correlations for HFCs and HCFCs. *J. Tsinghua Univ.* **2000**, *40* (10), 80−83.

Received for review October 29, 2003. Accepted December 15, 2003. This work was supported by the National Natural Science Foundation of China (No. 50225622) and the Fok Ying Tung Education Foundation (No. 81051).

JE0342163