Articles

Measurements of the Surface Tension for the R290 + R32 Mixture[†]

Katsuyuki Tanaka* **and Yukihiro Higashi**

Department of Mechanical Systems and Design Engineering, Iwaki Meisei University, Iwaki, Fukushima 970-8551, Japan

There were no data of the surface tension for the R290 + R32 mixture which is expected as one of the new refrigerant mixtures, and its prediction is considered to be difficult because it is a mixture of a very polar molecule with a nonpolar molecule. In this work, the surface tension measurements for the R290 + R32 mixture were carried out by the differential capillary-rise method modified for measuring mixtures. Thirty-one, thirty-five, and thirty-three data points were obtained with changing the composition of the mixture at $T = 280$ K, 290 K, and 300 K, respectively. The experimental uncertainties of temperature and surface tension are estimated to be within 20 mK and 0.2 $\text{mN}\cdot\text{m}^{-1}$, respectively. The excess molar surface tension is also calculated by the present data, and its uncertainty was estimated to be 0.3 $\text{mN}\cdot\text{m}^{-1}$. The excess molar surface tension was correlated as a function of composition. The deviation of the present data from the present correlation was within the experimental uncertainty.

Introduction

Regarding the working fluids of refrigerators and heat pump systems, hydrofluorocarbons and their mixtures are shifting toward hydrocarbons such as R290 (propane: C_3H_8) and R600a (isobutane: i-C_4H_{10}) from viewpoints of ozone depletion and global warming. Although hydrocarbons have no ozone depletion potential and no global warming potential, their applications in home refrigerator and air-conditioning are problematic because of their flammability. Whereas R32 (difluoromethane: CH_2F_2) is a kind of hydrofluorocarbon, it has a low global warming potential and is superior as a refrigerant. The mixing of R32 with hydrocarbons is effective in their applications.

In recent years, thermophysical properties for mixtures composed of R290, R600a, and R32 have been measured in our laboratory. Vapor−liquid equilibrium measurements of their three binary mixtures,[1−3] critical parameters, and saturated density measurements of their three binary mixtures,[4−6] and surface tension measurement of the R290 + R600a mixture[7] were conducted.

The surface tension, which is one of the important thermophysical properties of fluids, is required for the heat transfer solutions with boiling and condensation states. Its experimental data are necessary to refine the model for evaluating refrigerant mixtures and for designing refrigeration cycles. However, there were no data for this mixture.

In the present study, the surface tension of the R290 + R32 mixture has been measured by the differential capillary-rise method modified for measuring the mixture. Measurements are conducted at $T = 280$ K, 290 K, and 300 K with changing the composition of the mixture, and the excess molar surface tensions are calculated and correlated as a function of composition.

Apparatus

The surface tension measurement for fluid mixtures was already conducted for the R290 + R600a system in our laboratory, and the apparatus and procedure are described in detail there.[7] The apparatus was designed to measure the surface tension of the fluid mixture by the differential capillary-rise method. Two glass capillaries are placed vertically in a pressure vessel composed of a thick-walled Pyrex glass tube. Their inner radii of capillaries determined by means of a mercury thread are (0.4222 ± 0.0009) mm and (1.0050 ± 0.0012) mm. The sample is put in the pressure vessel whose temperature is kept constant to be within 10 mK by the thermostat. Temperature was measured with a 100 Ω platinum resistance thermometer with the thermometer bridge [ASL F250A] installed in the thermostat. It is calibrated against ITS-90 using a 25 Ω standard platinum resistance thermometer with the thermometer bridge [ASL F17A]. The experimental uncertainty of the temperature measurement is estimated to be within 20 mK. The second component of the mixture can be added to the pressure vessel for measurements at other compositions of the mixture. The pressure of the sample was measured by the precise digital pressure gauge [Paroscientific 2400A] to determine the composition of the sample from the vapor−liquid equilibrium relation. REFPROP[8] ver.8.0 was used for calculations of vapor−liquid equilibrium relation. The experimental uncertainty of the pressure measurement is estimated to be within 0.02 %. The location of the bottom of the meniscus of the sample in each capillary is measured by the traveling microscope through the window of the thermostat. Measured values of the location of the meniscus were corrected by the Rayleigh equation.[9] The corrected values were used for the difference of rise heights in the capillaries. The surface tension is determined by the following relation

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

where the local gravitational acceleration g at Iwaki, Japan, is

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* To whom correspondence should be addressed. E-mail: ktanaka@iwakimu.ac.jp. Tel.: +81-246-29-7026. Fax: +81-246-29-0577.

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Table 1. Experimental Surface Tensions for the R290 + R32 Mixture at T = 280.00 K

T / K	P / kPa	$h_1 - h_2$ / mm	x_{R290} / mol·mol^{-1}	σ / mN·m^{-1}	a^2 / mm^2
280.00	1034.61	2.76	0.010	9.7	2.01
	1043.03	2.67	0.013	9.4	1.95
	1099.68	2.78	0.037	9.5	2.03
	1159.63	2.75	0.070	9.0	2.00
	1184.36	2.70	0.087	8.7	1.96
	1190.67	2.61	0.092	8.4	1.90
	1217.40	2.72	0.115	8.5	1.98
	1222.01	2.69	0.120	8.4	1.96
	1223.07	2.58	0.121	8.0	1.88
	1224.52	2.64	0.123	8.2	1.92
	1225.61	2.64	0.124	8.2	1.92
	1232.43	2.58	0.131	7.9	1.88
	1240.57	2.65	0.141	8.0	1.92
	1281.92	2.89	0.515	6.4	2.10
	1263.20	3.09	0.588	6.5	2.25
	1257.52	3.10	0.605	6.5	2.26
	1239.90	3.32	0.648	6.8	2.41
	1239.68	3.30	0.648	6.7	2.40
	1232.84	3.35	0.662	6.8	2.44
	1221.87	3.41	0.682	6.8	2.48
	1212.24	3.53	0.697	7.0	2.57
	1206.12	3.57	0.706	7.1	2.60
	1189.23	3.63	0.729	7.1	2.64
	1166.11	3.81	0.755	7.4	2.77
	1144.97	3.87	0.775	7.4	2.81
	1097.55	4.09	0.813	7.8	2.98
	1077.66	4.12	0.826	7.8	3.00
	935.20	4.56	0.898	8.4	3.31
	842.18	4.82	0.931	8.8	3.51
	807.51	4.86	0.942	8.9	3.54
	715.86	5.02	0.968	9.1	3.65

Table 2. Experimental Surface Tensions for the R290 + R32 Mixture at T = 290.00 K

T / K	P / kPa	$h_1 - h_2$ / mm	x_{R290} / mol·mol^{-1}	σ / mN·m^{-1}	a^2 / mm^2
290.00	1355.46	2.39	0.002	8.1	1.74
	1359.27	2.35	0.003	8.0	1.71
	1363.25	2.35	0.004	8.0	1.71
	1467.28	2.34	0.005	7.9	1.70
	1461.54	2.32	0.039	7.5	1.69
	1517.47	2.30	0.065	7.2	1.67
	1542.83	2.25	0.078	7.0	1.64
	1547.85	2.34	0.081	7.2	1.70
	1561.57	2.32	0.090	7.1	1.69
	1569.39	2.27	0.095	6.9	1.65
	1572.52	2.27	0.097	6.9	1.65
	1593.54	2.22	0.114	6.6	1.62
	1627.26	2.29	0.143	6.5	1.66
	1639.45	2.23	0.156	6.3	1.63
	1653.88	2.14	0.175	5.9	1.56
	1660.57	2.17	0.185	5.9	1.58
	1668.21	2.24	0.198	6.0	1.63
	1673.93	2.12	0.209	5.7	1.54
	1678.30	2.39	0.485	5.0	1.74
	1672.01	2.38	0.506	4.9	1.73
	1665.23	2.44	0.525	5.0	1.77
	1659.83	2.53	0.539	5.1	1.84
	1641.39	2.55	0.580	5.1	1.86
	1633.21	2.60	0.596	5.1	1.89
	1628.53	2.68	0.604	5.2	1.95
	1599.99	2.92	0.648	5.6	2.13
	1564.36	3.11	0.691	5.9	2.27
	1475.11	3.33	0.768	6.1	2.42
	1414.83	3.54	0.805	6.4	2.58
	1199.39	3.97	0.896	7.0	2.89
	1131.63	4.17	0.917	7.3	3.03
	1102.98	4.22	0.925	7.4	3.07
	897.69	4.44	0.975	7.7	3.23
	841.43	4.55	0.986	7.9	3.31
	773.92	4.63	0.999	8.1	3.37

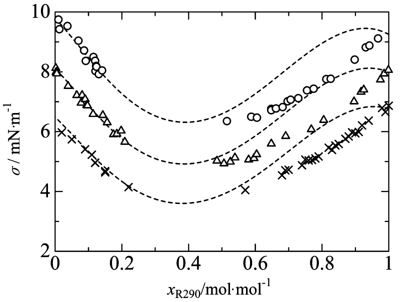

Figure 1. Surface tension results for the R290 + R32 mixture with relation to mole fraction of R290: ○, present data at T = 280.00 K; Δ, present data at T = 290.00 K; ×, present data at T = 300.00 K; ---, REFPROP[8] ver.8.0.

9.8002 m·s^{-2}. The contact angle θ is assumed to be zero based on the visual observation of the image magnified in the CRT monitor. Saturated densities ρ' and ρ'' are obtained from the calculations by the REFPROP ver.8.0. The experimental uncertainty of the surface tension measurement is estimated to be within 0.2 mN·m^{-1}.

The sample of R290 was supplied from Takachiho Chemical Industrial Co., Ltd., Japan. The purity of R290 was better than 99.9 mol %. The sample of R32 was supplied from Daikin Industrial Co., Ltd., Japan. The purity of R32 was better than 99.9999 mol %.

Experimental Results and Discussion

Thirty-one, thirty-five, and thirty-three data points of the surface tension against compositions were obtained on three isotherms of T = 280.00 K, 290.00 K, and 300.00 K, respectively. These data are listed in Tables 1 to 3. The capillary constant a^2 as expressed in eq 2 is also listed in Tables 1 to 3.

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

where g_n denotes the normal gravitational acceleration of 9.80665 m·s^{-2}. The surface tension for the R290 + R32 mixture with relation to mole fraction of R290 was shown in Figure 1. The data in the mole fraction range from 0.2 to 0.5 of R290 could not be obtained. In this range, this mixture shows a strong positive pressure azeotrope, and the pressure becomes flat against mole fraction. So it was difficult to blend the secondary sample into near azeotrope compositions. From the measurements in this work, it is revealed that the behavior of the composition dependence of the surface tension for the R290 + R32 mixture shows simply convex downward. Calculations by the REFPROP ver.8.0 are also plotted in Figure 1 as broken lines. The model of Moldover and Rainwater[10] is used in the REFPROP. The REFPROP calculations also show similar behavior. The present data at the R32-rich compositions are in good agreement with the REFPROP calculations, but the REFPROP calculations are larger up to about 1 mN·m^{-1} than the present data at the R290-rich compositions. The present data will be incorporated for improvement of the model of the surface tension mixture.

The excess molar surface tension σ_m^E was also calculated from eq 3 for the binary mixtures and shown in Figure 2.

$$\sigma_m^E = \sigma_m - (x_1\sigma_1 + x_2\sigma_2) \tag{3}$$

where 1, 2, and m refer to R290 of a first pure component, R32 of a second pure component, and mixture, respectively. The

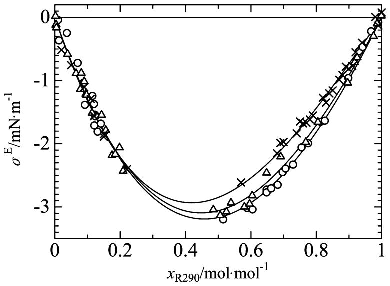

Figure 2. Excess molar surface tension for the R290 + R32 mixture with relation to mole fraction of R290: ○, present data at T = 280.00 K; Δ, present data at T = 290.00 K; ×, present data at T = 300.00 K; −, eq 4.

Table 3. Experimental Surface Tensions for the R290 + R32 Mixture at T = 300.00 K

T	P	$h_1 - h_2$	x_{R290}	σ	a^2
K	kPa	mm	mol·mol^{-1}	mN·m^{-1}	mm^2
300.00	1839.91	1.91	0.020	6.0	1.39
	1909.67	1.89	0.045	5.7	1.38
	1999.70	1.88	0.087	5.4	1.37
	2037.48	1.88	0.110	5.2	1.36
	2052.59	1.80	0.120	5.0	1.31
	2057.09	1.81	0.124	5.0	1.32
	2105.88	1.75	0.149	4.6	1.27
	2092.64	1.77	0.154	4.7	1.29
	2140.52	1.69	0.220	4.1	1.23
	2093.35	2.19	0.573	4.0	1.59
	1989.33	2.59	0.682	4.5	1.88
	1948.11	2.68	0.692	4.7	1.95
	1933.25	2.70	0.703	4.7	1.96
	1897.92	2.83	0.744	4.9	2.06
	1863.74	2.93	0.748	5.1	2.13
	1840.87	2.93	0.761	5.0	2.13
	1820.31	2.94	0.771	5.1	2.14
	1824.77	3.00	0.782	5.1	2.18
	1783.29	3.03	0.790	5.2	2.20
	1704.57	3.22	0.824	5.5	2.34
	1728.90	3.20	0.834	5.4	2.33
	1666.58	3.27	0.838	5.5	2.38
	1628.50	3.31	0.852	5.6	2.41
	1588.51	3.42	0.865	5.8	2.49
	1537.91	3.47	0.881	5.8	2.53
	1497.46	3.56	0.893	6.0	2.59
	1482.54	3.54	0.897	5.9	2.58
	1430.99	3.58	0.911	6.0	2.60
	1404.09	3.71	0.918	6.2	2.70
	1319.76	3.81	0.938	6.4	2.77
	1106.05	4.07	0.982	6.8	2.96
	1031.29	3.99	0.994	6.7	2.90
	1002.83	4.11	0.999	6.9	2.99

values of surface tension for pure R32 and R290 were obtained from our previous work.[11,12] The uncertainty of the excess molar surface tension was estimated to be 0.3 mN·m^{-1} in consideration of the uncertainty of the surface tension for pure components, 0.1 mN·m^{-1}. As shown in Figure 2, all of the σ_m^E values for this system are negative. At the R32-rich compositions, the σ_m^E values are almost the same at all temperatures. At the R290-rich compositions, those absolute values decrease with increasing temperature. The present σ_m^E data were correlated with the following polynomial-type Redlich−Kister equation[13]

$$\sigma_m^E = x_1 x_2 \sum_{i=0}^{1} A_i (1 - 2x_1)^i \qquad (4)$$

where A_i denotes the adjustable parameters determined by the present data. The parameters A_0 and A_1 and the standard deviations STD are given in Table 4. The solid lines in Figure 2 are calculations from eq 4. The deviations of the σ_m^E value from the present correlation were within the experimental uncertainty as shown in Figure 3.

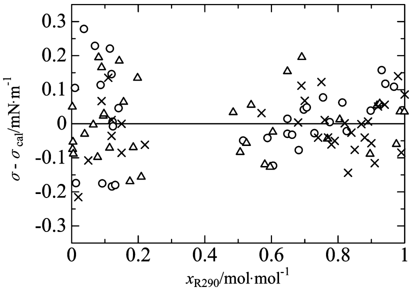

Figure 3. Deviation of the excess molar surface tension from eq 4 for the R290 + R32 mixture with relation to mole fraction of R290: ○, present data at T = 280.00 K; Δ, present data at T = 290.00 K; ×, present data at T = 300.00 K.

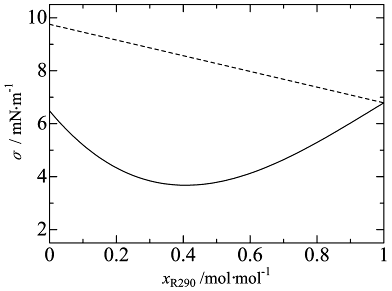

Figure 4. Comparison of the composition dependence of the surface tension at 300 K from correlations for the R290 + R32 mixture and the R290 + R600a mixture[7] with relation to mole fraction of R290: −, R290 + R32; ---, R290 + R600a.

Table 4. Parameters A_i of Equation 4 and Standard Deviations STD of the Excess Molar Surface Tension for Isotherms

T/K	A_0	A_1	STD/mN·m^{-1}
280.00	−12.669	−2.2188	0.12
290.00	−12.239	−2.6270	0.10
300.00	−11.396	−4.0371	0.08

The composition dependence of the surface tension for the R290 + R32 mixture and the R290 + R600a mixture[7] is shown in Figure 4. That for the R290 + R600a mixture could be represented as the simple linear function against mole fraction. However, that for the R290 + R32 mixture is not linear and became concave. These behaviors denote the same tendency of the critical temperature for these mixtures.[6]

Conclusion

The surface tension of the R290 + R32 mixture was measured on three isotherms of 280.00 K, 290.00 K, and 300.00 K. The composition dependence of the surface tension for this mixture was revealed. The correlation of the excess molar surface tension was formulated based on the present data and can be represented within the experimental uncertainty.

Acknowledgment

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