Surface Tension of Difluoromethane (R-32) + 1,1,1,2,3,3,3-Heptafluoropropane (R-227ea) from (253 to 333) K

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The surface tension of difluoromethane (R-32) (1) + 1,1,1,2,3,3,3-heptafluoropropane (R-227ea) (2) binary mixtures was measured at five nominal mass fractions of $w_1' = 0.3083$, 0.3639, 0.4064, 0.5519, and 0.7345 over the temperature range from (253 to 333) K using the differential capillary rise method (DCRM) under vapor-liquid equilibrium conditions. The temperature and surface tension uncertainties were estimated to be within ± 10 mK and ± 0.15 mN·m⁻¹, respectively. A new correlation based on the mass fraction was developed to represent the surface tension in the R-32 + R-227ea system.

Introduction

Ozone layer depletion and global warming caused by CFC and HCFC refrigerants have become a worldwide issue. Hydrofluorocarbon (HFC) mixtures are expected to become interim and long-term replacements for HCFC refrigerants (such as R-22) and R-502. Surface tension is a basic thermophysical property that influences heat transfer, and its quantification is important in the analysis of heat transfer through the vapor-liquid interface.

This paper presents surface tension measurements for binary mixtures of difluoromethane (R-32) + 1,1,1,2,3,3,3heptafluoropropane (R-227ea) at five nominal mass fractions in the temperature range from (253 to 333) K. The traditional correlation¹ cannot represent the experimental surface tension data of R-32 + R-227ea well, and the data were used to develop a correlation for R-32 + R-227ea mixtures as a function of the mass fraction based on the surface tension correlations of pure R-32 and R-227ea.

Experimental Section

Mixture Preparation. R-32 was obtained from Zhejiang Fluoro-Chemical Technology Research Institute and was used without further purification. The manufacturer stated that the purity was more than 99.95 mass %. The sample of R-227ea was obtained from Shanghai Huiyou Chemical Corp. and was used without further purification. The manufacturer stated that the purity was better than 99.9 mol % and the water content was less than 20 ppm. Before use, the R-32 and R-227ea samples in the sample bottles were frozen with liquefied nitrogen, and the vapor space was evacuated with a vacuum pump (KYKY FD110) to remove possible air impurities. A gas chromatograph (Lunan SP-6800A) with a thermal conductivity detector (TCD) and an ODPN (β , β -oxydipropionitrile) column was used to examine the deaerated samples, and the impurities were found to be less than 0.03% for both samples on the basis of the area response of the TCD.

The mixtures were gravimetrically prepared using an accurate electronic balance with a resolution of ± 0.001 g. Five R-32 (1) + R-227ea (2) binary mixtures were prepared

| Table 1. Experimental Surface Tension Data and |
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| Capillary Constants for Nominal Mass Fraction $w_1' =$ |
| 0.3083 for R-32 (1) + R-227ea (2) with Liquid Mass |
| Fraction w_1 |

| | | | | a^2/mm^2 | | σ/mN | $\cdot m^{-1}$ |
|--------|------------------------------------|------------------------------------|--------|------------|--------|--------|----------------|
| T/K | $\rho_{\rm l}/\rm kg{\cdot}m^{-3}$ | $\rho_{\rm v}/\rm kg{\cdot}m^{-3}$ | w_1 | (3, 2) | (3, 1) | (3, 2) | (3, 1) |
| 252.82 | 1368.7 | 10.6 | 0.3003 | 1.865 | 1.865 | 12.41 | 12.41 |
| 255.10 | 1360.8 | 11.6 | 0.2998 | 1.837 | 1.834 | 12.14 | 12.13 |
| 257.10 | 1353.7 | 12.5 | 0.2993 | 1.791 | 1.794 | 11.77 | 11.79 |
| 259.00 | 1347.0 | 13.3 | 0.2988 | 1.763 | 1.761 | 11.52 | 11.51 |
| 261.01 | 1339.9 | 14.3 | 0.2982 | 1.739 | 1.740 | 11.30 | 11.30 |
| 262.75 | 1333.7 | 15.3 | 0.2977 | 1.703 | 1.698 | 11.00 | 10.97 |
| 264.96 | 1325.7 | 16.5 | 0.2970 | 1.660 | 1.660 | 10.65 | 10.65 |
| 266.51 | 1320.0 | 17.4 | 0.2966 | 1.632 | 1.636 | 10.42 | 10.44 |
| 268.37 | 1313.2 | 18.5 | 0.2960 | 1.608 | 1.612 | 10.20 | 10.23 |
| 270.81 | 1304.1 | 20.1 | 0.2952 | 1.562 | 1.568 | 9.83 | 9.86 |
| 272.90 | 1296.2 | 21.6 | 0.2945 | 1.531 | 1.537 | 9.56 | 9.60 |
| 275.16 | 1287.6 | 23.3 | 0.2937 | 1.499 | 1.502 | 9.29 | 9.31 |
| 276.85 | 1281.1 | 24.6 | 0.2931 | 1.464 | 1.470 | 9.01 | 9.05 |
| 279.42 | 1271.1 | 26.7 | 0.2921 | 1.428 | 1.428 | 8.71 | 8.71 |
| 281.51 | 1262.8 | 28.6 | 0.2913 | 1.388 | 1.388 | 8.39 | 8.39 |
| 283.11 | 1256.4 | 30.1 | 0.2907 | 1.365 | 1.365 | 8.20 | 8.20 |
| 285.24 | 1247.7 | 32.1 | 0.2898 | 1.332 | 1.327 | 7.93 | 7.90 |
| 286.86 | 1241.1 | 33.8 | 0.2891 | 1.310 | 1.303 | 7.75 | 7.71 |
| 289.37 | 1230.6 | 36.5 | 0.2880 | 1.266 | 1.266 | 7.41 | 7.41 |
| 289.68 | 1229.3 | 36.9 | 0.2879 | 1.248 | 1.247 | 7.29 | 7.29 |
| 291.25 | 1222.7 | 38.7 | 0.2872 | 1.227 | 1.227 | 7.12 | 7.12 |
| 291.53 | 1221.4 | 39.0 | 0.2871 | 1.220 | 1.217 | 7.07 | 7.05 |
| 293.10 | 1214.7 | 40.9 | 0.2864 | 1.195 | 1.195 | 6.87 | 6.87 |
| 293.46 | 1213.1 | 41.4 | 0.2862 | 1.186 | 1.183 | 6.81 | 6.79 |
| 295.43 | 1204.5 | 43.9 | 0.2853 | 1.152 | 1.152 | 6.55 | 6.55 |
| 295.48 | 1204.5 | 43.9 | 0.2853 | 1.148 | 1.148 | 6.53 | 6.53 |
| 297.42 | 1195.6 | 46.6 | 0.2844 | 1.128 | 1.122 | 6.35 | 6.32 |
| 299.22 | 1187.5 | 49.2 | 0.2835 | 1.099 | 1.093 | 6.13 | 6.10 |
| 301.41 | 1177.4 | 52.5 | 0.2825 | 1.053 | 1.056 | 5.80 | 5.82 |
| 303.46 | 1167.7 | 55.8 | 0.2815 | 1.019 | 1.018 | 5.55 | 5.55 |
| 305.28 | 1159.0 | 58.9 | 0.2805 | 0.992 | 0.997 | 5.35 | 5.37 |
| 307.96 | 1145.8 | 63.8 | 0.2792 | 0.951 | 0.952 | 5.04 | 5.05 |
| 309.34 | 1138.8 | 66.4 | 0.2785 | 0.927 | 0.923 | 4.87 | 4.85 |
| 311.62 | 1127.1 | 71.0 | 0.2773 | 0.887 | 0.880 | 4.59 | 4.55 |
| 313.22 | 1118.7 | 74.4 | 0.2764 | 0.863 | 0.863 | 4.42 | 4.42 |
| 315.43 | 1106.8 | 79.4 | 0.2752 | 0.823 | 0.820 | 4.14 | 4.13 |
| 317.43 | 1095.7 | 84.2 | 0.2742 | 0.788 | 0.785 | 3.91 | 3.89 |
| 319.58 | 1083.4 | 89.8 | 0.2730 | 0.759 | 0.754 | 3.70 | 3.67 |
| 321.54 | 1071.9 | 95.1 | 0.2719 | 0.720 | 0.714 | 3.45 | 3.42 |
| 323.69 | 1058.8 | 101.4 | 0.2707 | 0.681 | 0.681 | 3.19 | 3.19 |
| 325.42 | 1048.0 | 106.9 | 0.2697 | 0.641 | 0.640 | 2.96 | 2.95 |
| 327.16 | 1036.6 | 112.6 | 0.2688 | 0.618 | 0.615 | 2.80 | 2.78 |
| 329.37 | 1021.7 | 120.5 | 0.2676 | 0.589 | 0.587 | 2.60 | 2.59 |
| 331.65 | 1005.6 | 129.3 | 0.2663 | 0.549 | 0.551 | 2.36 | 2.37 |
| 333.37 | 992.8 | 136.5 | 0.2654 | 0.521 | 0.521 | 2.19 | 2.19 |

at nominal mass fractions (the liquid and vapor average composition) of $w_1' = 0.3083$, 0.3639, 0.4064, 0.5519, and 0.7345.

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| Table 2. Experimental Surface Tension Data and |
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| Capillary Constants for Nominal Mass Fraction $w_1' =$ |
| 0.3639 for R-32 (1) + R-227ea (2) with Liquid Mass |
| Fraction w_1 |

| | | | | a^2/mm^2 | | $\sigma/mN\cdot m^{-1}$ | |
|-------------|---|------------------------------------|--------|-------------------|--------|-------------------------|--------|
| <i>T</i> /K | $ ho_{\rm l}/{\rm kg}{\cdot}{\rm m}^{-3}$ | $\rho_{\rm v}/\rm kg{\cdot}m^{-3}$ | w_1 | (3, 2) | (3, 1) | (3, 2) | (3, 1) |
| 256.92 | 1329.5 | 12.5 | 0.3540 | 1.837 | 1.837 | 11.85 | 11.85 |
| 260.89 | 1315.6 | 14.4 | 0.3528 | 1.766 | 1.764 | 11.26 | 11.25 |
| 262.79 | 1308.9 | 15.4 | 0.3521 | 1.745 | 1.745 | 11.06 | 11.06 |
| 264.88 | 1301.3 | 16.6 | 0.3514 | 1.701 | 1.707 | 10.71 | 10.75 |
| 266.88 | 1294.1 | 17.8 | 0.3507 | 1.670 | 1.674 | 10.44 | 10.47 |
| 268.79 | 1287.1 | 19.0 | 0.3500 | 1.641 | 1.647 | 10.20 | 10.23 |
| 270.78 | 1279.7 | 20.3 | 0.3493 | 1.607 | 1.608 | 9.92 | 9.92 |
| 273.60 | 1269.3 | 22.2 | 0.3482 | 1.557 | 1.557 | 9.51 | 9.51 |
| 275.50 | 1262.0 | 23.7 | 0.3474 | 1.514 | 1.521 | 9.19 | 9.23 |
| 277.39 | 1254.7 | 25.2 | 0.3466 | 1.485 | 1.490 | 8.95 | 8.98 |
| 279.46 | 1246.7 | 26.9 | 0.3457 | 1.451 | 1.451 | 8.67 | 8.67 |
| 281.45 | 1238.8 | 28.7 | 0.3448 | 1.416 | 1.419 | 8.40 | 8.41 |
| 283.49 | 1230.7 | 30.6 | 0.3439 | 1.383 | 1.383 | 8.13 | 8.13 |
| 285.46 | 1222.7 | 32.6 | 0.3430 | 1.362 | 1.363 | 7.94 | 7.95 |
| 287.47 | 1214.5 | 34.7 | 0.3420 | 1.310 | 1.309 | 7.57 | 7.57 |
| 289.37 | 1206.6 | 36.8 | 0.3411 | 1.280 | 1.287 | 7.34 | 7.38 |
| 291.47 | 1197.7 | 39.2 | 0.3400 | 1.258 | 1.258 | 7.14 | 7.14 |
| 293.20 | 1190.3 | 41.3 | 0.3391 | 1.214 | 1.221 | 6.83 | 6.87 |
| 295.16 | 1181.8 | 43.8 | 0.3381 | 1.183 | 1.184 | 6.60 | 6.60 |
| 296.82 | 1174.4 | 46.1 | 0.3372 | 1.150 | 1.150 | 6.36 | 6.36 |
| 297.86 | 1169.8 | 47.6 | 0.3366 | 1.129 | 1.129 | 6.21 | 6.21 |
| 299.29 | 1163.3 | 49.6 | 0.3358 | 1.110 | 1.112 | 6.06 | 6.07 |
| 301.27 | 1154.3 | 52.7 | 0.3346 | 1.067 | 1.067 | 5.76 | 5.76 |
| 303.27 | 1144.9 | 55.9 | 0.3335 | 1.034 | 1.034 | 5.52 | 5.52 |
| 305.26 | 1135.3 | 59.3 | 0.3323 | 1.005 | 1.003 | 5.30 | 5.29 |
| 307.24 | 1125.7 | 62.8 | 0.3311 | 0.975 | 0.975 | 5.08 | 5.08 |
| 309.18 | 1116.0 | 66.5 | 0.3299 | 0.934 | 0.934 | 4.80 | 4.80 |
| 311.24 | 1105.4 | 70.7 | 0.3286 | 0.910 | 0.910 | 4.61 | 4.61 |
| 313.51 | 1093.5 | 75.6 | 0.3271 | 0.867 | 0.867 | 4.32 | 4.32 |
| 315.28 | 1083.9 | 79.7 | 0.3260 | 0.838 | 0.839 | 4.12 | 4.13 |
| 317.24 | 1073.1 | 84.4 | 0.3247 | 0.800 | 0.800 | 3.88 | 3.88 |
| 319.25 | 1061.6 | 89.6 | 0.3234 | 0.764 | 0.764 | 3.64 | 3.64 |
| 321.30 | 1049.5 | 95.3 | 0.3220 | 0.724 | 0.722 | 3.39 | 3.38 |
| 323.20 | 1038.0 | 100.9 | 0.3207 | 0.704 | 0.704 | 3.23 | 3.23 |
| 325.23 | 1025.2 | 107.3 | 0.3193 | 0.676 | 0.676 | 3.04 | 3.04 |
| 327.40 | 1010.9 | 114.6 | 0.3179 | 0.625 | 0.621 | 2.74 | 2.73 |
| 329.30 | 997.9 | 121.6 | 0.3166 | 0.592 | 0.592 | 2.54 | 2.54 |
| 331.57 | 981.7 | 130.5 | 0.3150 | 0.537 | 0.537 | 2.24 | 2.24 |
| 333 40 | 967.9 | 138.4 | 0.3138 | 0.507 | 0.506 | 2.06 | 2.06 |

Apparatus and Procedure. Surface tension was measured using the direct optical measurement system based on the differential capillary rise method. The apparatus and procedure have been described detailedly in previous work²⁻⁶ and are only briefly introduced here.

Before the experiment, the inner radii of three capillaries in the sample cell were recalibrated by partially filling the capillaries with mercury slugs of different masses before the measurements to give $r_1 = (0.3901 \pm 0.0002)$ mm, $r_2 =$ (0.2591 ± 0.0002) mm, and $r_3 = (0.1250 \pm 0.0003)$ mm. The temperatures were determined on the International Temperature Scale of 1990 (ITS-90). All of the temperature measurement equipment was calibrated by NIM (National Institute of Metrology, PR China) before the experiment. 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 gating switch (Tinsley 5840CS/6T), and a personal computer. 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 mobilizable telescope with an uncertainty of ± 10 μ m. The contact angle, θ , was assumed to be zero because the inner walls of the capillaries were carefully washed before the measurements.

All of the measurements were independently carried out under equilibrium conditions between the liquid and its saturated vapor. A total error analysis gave the estimated Table 3. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' = 0.4064$ for R-32 (1) + R-227ea (2) with Liquid Mass Fraction w_1

| | | | | a^2/n | nm ² | σ/mN | $\cdot m^{-1}$ |
|------------------|------------------------------------|------------------------------------|--------|---------|-----------------|--------------|----------------|
| T/K | $\rho_{\rm l}/\rm kg{\cdot}m^{-3}$ | $\rho_{\rm v}/\rm kg{\cdot}m^{-3}$ | w_1 | (3, 2) | (3, 1) | (3, 2) | (3, 1) |
| 252.66 | 1325.4 | 10.7 | 0.3988 | 1.978 | 1.983 | 12.74 | 12.77 |
| 254.68 | 1318.5 | 11.6 | 0.3983 | 1.928 | 1.932 | 12.35 | 12.37 |
| 257.10 | 1310.1 | 12.6 | 0.3977 | 1.891 | 1.892 | 12.02 | 12.03 |
| 258.88 | 1303.9 | 13.5 | 0.3972 | 1.856 | 1.856 | 11.74 | 11.74 |
| 261.05 | 1296.2 | 14.6 | 0.3966 | 1.829 | 1.828 | 11.49 | 11.48 |
| 262.85 | 1289.8 | 15.5 | 0.3961 | 1.784 | 1.784 | 11.14 | 11.14 |
| 262.98 | 1289.3 | 15.6 | 0.3961 | 1.785 | 1.791 | 11.14 | 11.18 |
| 264.87 | 1282.6 | 16.7 | 0.3955 | 1.757 | 1.761 | 10.90 | 10.92 |
| 267.04 | 1274.7 | 17.9 | 0.3948 | 1.705 | 1.709 | 10.50 | 10.52 |
| 268.72 | 1268.5 | 19.0 | 0.3943 | 1.688 | 1.688 | 10.33 | 10.33 |
| 270.70 | 1261.2 | 20.3 | 0.3936 | 1.654 | 1.650 | 10.06 | 10.03 |
| 273.15 | 1252.0 | 22.0 | 0.3928 | 1.600 | 1.603 | 9.64 | 9.66 |
| 275.30 | 1243.9 | 23.6 | 0.3920 | 1.548 | 1.553 | 9.26 | 9.29 |
| 277.27 | 1236.3 | 25.2 | 0.3913 | 1.520 | 1.526 | 9.02 | 9.06 |
| 279.60 | 1227.2 | 27.2 | 0.3904 | 1.486 | 1.489 | 8.74 | 8.76 |
| 281.21 | 1220.8 | 28.6 | 0.3898 | 1.446 | 1.449 | 8.45 | 8.46 |
| 283.17 | 1213.0 | 30.4 | 0.3890 | 1.421 | 1.421 | 8.23 | 8.23 |
| 285.19 | 1204.8 | 32.4 | 0.3882 | 1.381 | 1.390 | 7.93 | 7.99 |
| 286.62 | 1199.0 | 33.9 | 0.3876 | 1.365 | 1.365 | 7.79 | 7.79 |
| 289.42 | 1187.3 | 36.9 | 0.3863 | 1.322 | 1.322 | 7.45 | 7.45 |
| 290.16 | 1184.2 | 37.8 | 0.3860 | 1.281 | 1.281 | 7.20 | 7.20 |
| 291.50 | 1178.5 | 39.3 | 0.3854 | 1.263 | 1.260 | 7.05 | 7.03 |
| 291.66 | 1177.8 | 39.5 | 0.3853 | 1.268 | 1.275 | 7.07 | 7.11 |
| 293.80 | 1168.6 | 42.2 | 0.3843 | 1.209 | 1.212 | 6.67 | 6.69 |
| 293.83 | 1168.5 | 42.2 | 0.3843 | 1.221 | 1.221 | 6.74 | 6.74 |
| 296.02 | 1158.8 | 45.1 | 0.3832 | 1.175 | 1.172 | 6.41 | 6.40 |
| 297.36 | 1152.8 | 47.0 | 0.3826 | 1.145 | 1.145 | 6.20 | 6.20 |
| 299.17 | 1144.6 | 49.6 | 0.3817 | 1.120 | 1.121 | 6.01 | 6.01 |
| 301.75 | 1132.7 | 53.6 | 0.3803 | 1.071 | 1.076 | 5.66 | 5.69 |
| 303.33 | 1125.2 | 56.1 | 0.3795 | 1.048 | 1.057 | 5.49 | 5.54 |
| 305.17 | 1116.3 | 58.3 | 0.3785 | 1.031 | 1.029 | 5.35 | 5.33 |
| 307.23 | 1106.2 | 63.0 | 0.3774 | 0.980 | 0.990 | 5.01 | 5.06 |
| 309.63 | 1094.1 | 67.6 | 0.3761 | 0.920 | 0.928 | 4.63 | 4.67 |
| 311.26 | 1085.6 | 71.0 | 0.3752 | 0.896 | 0.901 | 4.45 | 4.48 |
| 313.21 | 1075.3 | 75.2 | 0.3740 | 0.869 | 0.862 | 4.26 | 4.22 |
| 315.30 | 1063.9 | 80.0 | 0.3728 | 0.843 | 0.849 | 4.06 | 4.09 |
| 318.29 | 1047.1 | 87.4 | 0.3710 | 0.771 | 0.770 | 3.63 | 3.62 |
| 319.03 | 1039.2 | 91.0 | 0.3702 | 0.703 | 0.703 | 3.00 | 3.00 |
| 321.27 | 1029.4 | 95.6 | 0.3692 | 0.720 | 0.720 | 3.29 | 3.29 |
| 323.76 | 1014.0 | 103.1 | 0.3677 | 0.679 | 0.674 | 3.03 | 3.01 |
| 020.29 997 91 | 1004.1 | 108.0 | 0.3008 | 0.604 | 0.000 | 2.80 | 2.80 |
| 990 44 | 990.0 | 114.9 | 0.3030 | 0.004 | 0.002 | 2.09 | 2.08 |
| 029.44 991 79 | 910.0 | 122.9 | 0.3043 | 0.520 | 0.002 | 2.45 9.15 | 2.45 |
| 331.73 999.40 | 909.U | 132.1 | 0.3629 | 0.030 | 0.031 | 2.15 | 2.15 |
| əəə.4ð | 940.0 | 199.9 | 0.9019 | 0.495 | 0.490 | 1.90 | 1.99 |

surface tension uncertainty to be within $\pm 0.15 \text{ mN} \cdot \text{m}^{-1}$. The binary mixture preparation procedure has been described in previous work.^{3–6} An accurate electronic balance with a resolution of $\pm 0.001 \text{ g}$ (Mettler Toledo PR1203) and a turbomolecular pump (KYKY FD110) with a highest vacuum of 1×10^{-6} Pa were used to prepare the mixtures. The mixture nominal mass fraction uncertainty was estimated to be better than $\pm 0.01 \text{ mass } \%$.

The R-32 (1) + R-227ea (2) mixtures at the five nominal mass fractions w_1 of 0.3083, 0.3639, 0.5519, 0.4064, and 0.7345 are zeotropic, so the coexisting liquid and vapor compositions differed. The mass fraction 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 obatained from NIST REFPROP 7.1.7 The liquid height was also measured to check the precision of the calculation for the mass fraction. The gas-phase composition was analyzed using a gas chromatograph (Lunan SP-6800A) with a thermal conductivity detector (TCD) and an ODPN column after the surface tension measurements to verify the calculation. The detector response was carefully calibrated using gravimetrically prepared mixtures. The difference between the measured compositions and the calculated compositions are within ±0.002 mass.

Table 4. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' =$ 0.5519 for R-32 (1) + R-227ea (2) with Liquid Mass Fraction w_1

| | | | | a^2/mm^2 | | σ/mN | $\cdot m^{-1}$ |
|-------------|------------------------------------|--|--------|-------------------|--------|--------|----------------|
| <i>T</i> /K | $\rho_{\rm l}/\rm kg{\cdot}m^{-3}$ | $\rho_{\rm v}/{\rm kg}{\cdot}{\rm m}^{-3}$ | w_1 | (3, 2) | (3, 1) | (3, 2) | (3, 1) |
| 254.83 | 1260.7 | 11.8 | 0.5440 | 2.077 | 2.077 | 12.71 | 12.71 |
| 257.09 | 1253.1 | 12.8 | 0.5434 | 2.035 | 2.037 | 12.37 | 12.38 |
| 258.83 | 1247.1 | 13.6 | 0.5429 | 1.980 | 1.980 | 11.97 | 11.97 |
| 260.99 | 1239.7 | 14.7 | 0.5423 | 1.941 | 1.941 | 11.65 | 11.65 |
| 262.96 | 1232.8 | 15.7 | 0.5417 | 1.901 | 1.901 | 11.34 | 11.34 |
| 264.68 | 1226.8 | 16.7 | 0.5412 | 1.874 | 1.870 | 11.11 | 11.09 |
| 266.75 | 1219.5 | 17.9 | 0.5405 | 1.825 | 1.824 | 10.75 | 10.74 |
| 268.37 | 1213.7 | 18.9 | 0.5400 | 1.799 | 1.797 | 10.53 | 10.52 |
| 270.78 | 1204.9 | 20.5 | 0.5392 | 1.740 | 1.740 | 10.10 | 10.10 |
| 273.15 | 1196.2 | 22.1 | 0.5383 | 1.691 | 1.691 | 9.73 | 9.73 |
| 275.48 | 1187.6 | 23.9 | 0.5375 | 1.656 | 1.655 | 9.44 | 9.44 |
| 277.43 | 1180.2 | 25.4 | 0.5367 | 1.641 | 1.641 | 9.29 | 9.29 |
| 279.43 | 1172.6 | 27.1 | 0.5359 | 1.590 | 1.590 | 8.92 | 8.92 |
| 281.30 | 1165.4 | 28.7 | 0.5351 | 1.553 | 1.551 | 8.65 | 8.64 |
| 283.30 | 1157.6 | 30.6 | 0.5342 | 1.520 | 1.522 | 8.39 | 8.40 |
| 284.67 | 1152.2 | 31.9 | 0.5336 | 1.465 | 1.471 | 8.04 | 8.07 |
| 287.63 | 1140.3 | 35.0 | 0.5322 | 1.419 | 1.428 | 7.69 | 7.73 |
| 289.31 | 1133.4 | 36.8 | 0.5314 | 1.385 | 1.387 | 7.44 | 7.45 |
| 291.47 | 1124.4 | 39.3 | 0.5304 | 1.341 | 1.350 | 7.13 | 7.18 |
| 291.67 | 1123.5 | 39.6 | 0.5303 | 1.352 | 1.349 | 7.18 | 7.16 |
| 293.53 | 1115.7 | 41.9 | 0.5293 | 1.312 | 1.311 | 6.90 | 6.90 |
| 295.61 | 1106.7 | 44.5 | 0.5282 | 1.255 | 1.255 | 6.53 | 6.53 |
| 297.68 | 1097.6 | 47.4 | 0.5271 | 1.223 | 1.223 | 6.29 | 6.29 |
| 299.80 | 1088.2 | 50.5 | 0.5259 | 1.188 | 1.185 | 6.04 | 6.03 |
| 301.58 | 1080.0 | 53.2 | 0.5249 | 1.149 | 1.146 | 5.78 | 5.77 |
| 303.87 | 1069.4 | 57.0 | 0.5235 | 1.104 | 1.097 | 5.48 | 5.44 |
| 306.29 | 1057.8 | 61.2 | 0.5221 | 1.056 | 1.050 | 5.16 | 5.13 |
| 307.39 | 1052.4 | 63.2 | 0.5214 | 1.020 | 1.019 | 4.94 | 4.94 |
| 309.81 | 1040.4 | 67.9 | 0.5198 | 0.974 | 0.972 | 4.64 | 4.63 |
| 311.74 | 1030.4 | 71.9 | 0.5186 | 0.933 | 0.928 | 4.38 | 4.36 |
| 313.35 | 1022.0 | 75.4 | 0.5175 | 0.895 | 0.898 | 4.15 | 4.17 |
| 315.61 | 1009.8 | 80.6 | 0.5159 | 0.853 | 0.853 | 3.88 | 3.88 |
| 317.69 | 998.2 | 85.8 | 0.5145 | 0.807 | 0.811 | 3.61 | 3.63 |
| 320.00 | 984.8 | 92.0 | 0.5129 | 0.761 | 0.760 | 3.33 | 3.32 |
| 321.42 | 976.4 | 96.0 | 0.5118 | 0.725 | 0.729 | 3.13 | 3.14 |
| 323.72 | 962.1 | 103.0 | 0.5102 | 0.694 | 0.693 | 2.92 | 2.92 |
| 325.89 | 948.1 | 110.1 | 0.5085 | 0.627 | 0.630 | 2.57 | 2.59 |
| 327.68 | 936.0 | 116.5 | 0.5072 | 0.590 | 0.593 | 2.37 | 2.38 |
| 329.35 | 924.3 | 122.8 | 0.5059 | 0.554 | 0.558 | 2.18 | 2.19 |
| 331.47 | 908.7 | 131.6 | 0.5043 | 0.527 | 0.527 | 2.01 | 2.01 |
| aaa aa | 892.0 | 140.9 | 0.0028 | 0.4/4 | 0.408 | 1.75 | 1.72 |

Results and Discussions

The surface tension can be calculated from

$$\sigma = \frac{(\rho_{\rm l} - \rho_{\rm v})g}{2} \frac{(h_1 - h_2)}{[(1/r_1) - (1/r_2)]} \tag{1}$$

where σ is the surface tension, g is the local gravitational acceleration in Beijing, China ($g = 9.8015 \text{ m}\cdot\text{s}^{-2}$), and $\rho_{\rm l}$ and $\rho_{\rm v}$ are the densities of the saturated liquid and vapor, respectively. $\rho_{\rm l}$ and $\rho_{\rm v}$ were calculated from NIST REF-PROP 7.1⁷ for the R-32 + R-227ea mixtures.

The height of the meniscus bottom in each capillary, h_0 , was measured, and the actual rise height h was calculated using the Rayleigh correlation⁸

$$h = h_0 + \frac{r}{3} - \frac{0.1288r^2}{h_0} + \frac{0.1312r^3}{h_0^2}$$
(2)

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

$$a^2 = \frac{h_1 - h_2}{(1/r_1) - (1/r_2)} \tag{3}$$

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 Table 5. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w_1' =$ 0.7345 for R-32 (1) + R-227ea (2) with Liquid Mass Fraction w_1

| | | | | a^2/mm^2 | | $\sigma/mN \cdot m^{-1}$ | |
|--------|---|---|--------|------------|--------|--------------------------|--------|
| T/K | $ ho_{\rm l}/{\rm kg}{\cdot}{\rm m}^{-3}$ | $\rho_{\rm v}/\rm kg{\scriptstyle \bullet}m^{-3}$ | w_1 | (3, 2) | (3, 1) | (3, 2) | (3, 1) |
| 258.84 | 1183.5 | 13.6 | 0.7282 | 2.203 | 2.206 | 12.63 | 12.65 |
| 262.80 | 1170.2 | 15.7 | 0.7274 | 2.142 | 2.135 | 12.12 | 12.08 |
| 264.66 | 1163.9 | 16.7 | 0.7270 | 2.069 | 2.067 | 11.63 | 11.62 |
| 268.63 | 1150.1 | 19.1 | 0.7261 | 1.993 | 1.984 | 11.05 | 11.00 |
| 272.17 | 1137.6 | 21.4 | 0.7252 | 1.897 | 1.897 | 10.38 | 10.38 |
| 272.91 | 1135.0 | 21.9 | 0.7249 | 1.885 | 1.884 | 10.28 | 10.28 |
| 275.50 | 1125.6 | 23.8 | 0.7242 | 1.829 | 1.832 | 9.87 | 9.89 |
| 277.30 | 1119.0 | 25.3 | 0.7237 | 1.803 | 1.801 | 9.66 | 9.65 |
| 279.39 | 1111.3 | 27.0 | 0.7231 | 1.755 | 1.758 | 9.32 | 9.34 |
| 281.54 | 1103.2 | 28.9 | 0.7224 | 1.690 | 1.696 | 8.90 | 8.93 |
| 283.29 | 1096.5 | 30.5 | 0.7219 | 1.645 | 1.649 | 8.59 | 8.61 |
| 285.18 | 1089.2 | 32.3 | 0.7212 | 1.616 | 1.617 | 8.37 | 8.37 |
| 289.33 | 1072.9 | 36.6 | 0.7197 | 1.532 | 1.532 | 7.78 | 7.78 |
| 289.89 | 1070.6 | 37.3 | 0.7195 | 1.492 | 1.487 | 7.55 | 7.53 |
| 291.93 | 1062.3 | 39.6 | 0.7187 | 1.463 | 1.467 | 7.33 | 7.35 |
| 293.53 | 1055.7 | 41.6 | 0.7181 | 1.421 | 1.426 | 7.06 | 7.09 |
| 293.91 | 1054.1 | 42.1 | 0.7179 | 1.419 | 1.421 | 7.04 | 7.05 |
| 295.50 | 1047.5 | 44.1 | 0.7173 | 1.385 | 1.389 | 6.81 | 6.83 |
| 299.50 | 1030.2 | 49.6 | 0.7156 | 1.284 | 1.284 | 6.17 | 6.17 |
| 301.63 | 1020.8 | 52.9 | 0.7146 | 1.243 | 1.243 | 5.90 | 5.90 |
| 303.55 | 1012.1 | 55.9 | 0.7137 | 1.193 | 1.193 | 5.59 | 5.59 |
| 305.75 | 1001.9 | 59.7 | 0.7126 | 1.157 | 1.157 | 5.34 | 5.34 |
| 307.36 | 994.2 | 65.5 | 0.7118 | 1.108 | 1.108 | 5.04 | 5.04 |
| 309.43 | 984.2 | 66.5 | 0.7107 | 1.046 | 1.046 | 4.70 | 4.70 |
| 311.28 | 975.0 | 70.2 | 0.7097 | 1.018 | 1.018 | 4.51 | 4.51 |
| 313.26 | 964.9 | 74.4 | 0.7086 | 0.968 | 0.968 | 4.22 | 4.22 |
| 315.39 | 953.7 | 79.2 | 0.7074 | 0.924 | 0.924 | 3.96 | 3.96 |
| 317.30 | 943.3 | 83.9 | 0.7064 | 0.879 | 0.879 | 3.70 | 3.70 |
| 319.52 | 930.9 | 89.6 | 0.7050 | 0.820 | 0.820 | 3.38 | 3.38 |
| 321.31 | 920.5 | 94.6 | 0.7039 | 0.771 | 0.771 | 3.12 | 3.12 |
| 323.50 | 907.3 | 101.1 | 0.7025 | 0.729 | 0.727 | 2.88 | 2.87 |
| 325.30 | 896.0 | 106.9 | 0.7013 | 0.680 | 0.680 | 2.63 | 2.63 |
| 327.31 | 882.9 | 113.8 | 0.7000 | 0.645 | 0.647 | 2.43 | 2.44 |
| 329.34 | 868.9 | 121.4 | 0.6987 | 0.587 | 0.589 | 2.15 | 2.16 |
| 331.61 | 852.5 | 130.7 | 0.6971 | 0.530 | 0.530 | 1.87 | 1.87 |
| 333.48 | 838.0 | 139.1 | 0.6959 | 0.476 | 0.475 | 1.63 | 1.63 |
| | | | | | | | |

1 to 5, as are the saturated liquid density, $\rho_{\rm l}$, the saturated vapor density, $\rho_{\rm v}$, the capillary constant, a^2 , and the mass fraction of R-32 (w_1) of liquid phases in the mixtures at each temperature.

Figures 1 and 2 show the capillary constant and surface tension variation for the R-32 + R-227ea mixtures and pure R-32 and pure R-227ea as a function of temperature. From Figure 1, the crossing point of the capillary constant for R-32 + R-227ea diverges from the point that the pure R-32and R-227ea focuses on. From Figure 2, the surface tension data of R-32 + R-227ea mixtures are out of the range between the surface tension of pure R-32 and R-227ea. The possible reason for this behavior is the interaction of different molecules. Because R-32 belongs to the derivatives of the methane family and R-227ea belongs to the derivatives of the propane family, there are large differences between the molecular structures of these two materials. If the saturated liquid and gas densities of mixtures calculated from NIST REFPROP 7.1⁷ is accurate enough, then the above results are believable because the experiment uncertainty was mostly considered in the experimental procedure. The surface tension of R-32 (1) + R-227ea (2) mixtures at nominal mass fractions $w_1' = 0.3083$, 0.4064, and 0.7345 was first measured. For a further determination of the experimental uncertainties, the experiment equipment including the radii of capillaries and the telescope was recalibrated. The calibrated capillary radii have good uniformity with the radii used before,³⁻⁶ and the uncertainty of the telescope was still $\pm 10 \ \mu m$ or less. One month later, the surface tension of R-32 (1) + R-227ea (2) mixtures at nominal mass fractions $w_1' =$ 0.3639 and 0.5519 was measured using this recalibrated



Figure 1. Capillary constant vs temperature of R-32 (1) + R-227ea (2): \Box , $w_1' = 0.3083$; \diamond , $w_1' = 0.3639$; \bigcirc , $w_1' = 0.4064$; \triangle , $w_1' = 0.5519$; \bigtriangledown , $w_1' = 0.7345$; -, R-32;⁹ - \cdot -, R-227ea.⁴



Figure 2. Surface tension vs temperature of R-32 (1) + R-227ea (2): \Box , $w_1' = 0.3083$; \diamond , $w_1' = 0.3639$; \bigcirc , $w_1' = 0.4064$; \triangle , $w_1' = 0.5519$; \bigtriangledown , $w_1' = 0.7345$; -, R-32;⁹ - · -, R-227ea.⁴

equipment. From Figures 1 and 2, the experimental results of five mixtures show good consistency.

The surface tension of a pure fluid 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. T and T_c are the temperature and the critical temperature, respectively. σ_0 and n for R-32 are set as 76.66 mN·m⁻¹ and 1.271, respectively.⁹ σ_0 and n for R-227ea are set as 51.99 mN·m⁻¹ and 1.273, respectively.⁴ The critical temperature for R-32 and R-227ea are 351.255 K¹⁰ and 375.95 K,¹¹ respectively.

The surface tension data of the R-32 + R-227ea system cannot be represented well by the traditional correlation used in previous work.^{3–6} On the basis of the van der Waals-type correlation of pure fluids and the traditional correlation, the surface tension of binary refrigerant mixtures can be represented as

$$\sigma = w_1 \sigma_1 + w_2 \sigma_2 + w_1 w_2 C + \sigma_1 w_1 w_2 (D + E w_1) \quad (5)$$

where σ_1 and σ_2 are the surface tension values of pure R-32 and R-227ea calculated using eq 4 and w_1 and w_2 are the liquid mass fractions. *C*, *D*, and *E* are coefficients that can be determined by fitting eq 5 to the present experimental data. Table 6 lists the coefficients and the average absolute and relative deviations. Figure 3 shows the absolute

Table 6. Coefficients in Equation 5 and Absolute andRelative Deviations between Experimental andCalculated Values

| mixture | $C/\mathrm{mN}\cdot\mathrm{m}^{-1}$ | D | Ε | $\bar{\delta}_{\rm a}/{\rm mN}\cdot{\rm m}^{-1a}$ | $\bar{\delta}_{ m r}$ /% ^b |
|---|--|-----------------------------|--------|---|---------------------------------------|
| equation 5 | -2.7677 | -0.1595 | 0.1710 | 0.048 | 0.95 |
| ^a $\bar{\delta}_{a} = \frac{1}{n}$ | $\sum_{i=1}^{n} \sigma_{\text{exptl},i} - \sigma $ | $\sigma_{\text{calcd},i}$; | | | |
| ^b $\delta_{\rm r} = \frac{1}{n}$ | $\sum_{i=1}^{n} \frac{ \sigma_{\text{exptl},i} - \sigma_{\text{calce}} }{\sigma_{\text{calce}}}$ | $\sigma_{\text{calcd},i}$ | | | |



Figure 3. Absolute deviations of experimental surface tension data of R-32 (1) + R-227ea (2) from eq 5: \Box , $w_1' = 0.3083$; \Diamond , $w_1' = 0.3639$; \bigcirc , $w_1' = 0.4064$; \triangle , $w_1' = 0.5519$; \bigtriangledown , $w_1' = 0.7345$.

deviations of the present data from eq 5 for R-32 (1) + R-227ea (2) mixtures with various mass fractions. The results in Figure 3 show that the absolute deviations of the present data from eq 5 are less than ± 0.15 mN·m⁻¹, which is consistent with the experimental uncertainty.

Conclusions

The surface tension of the binary mixture R-32 + R-227ea was measured at five nominal mass fractions over the temperature range from (253 to 333) K using the DCRM method under vapor—liquid equilibrium conditions. The temperature and surface tension uncertainties were estimated to be within ± 10 mK and ± 0.15 mN·m⁻¹, respectively. The traditional correlation cannot represent the surface tension data of the R-32 + R-227ea system well, and a new correlation was developed to represent the surface tension data.

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