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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

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The surface tensions of binary mixtures of difluoromethane (R-32) + 1,1,1,2-tetrafluoroethane (R-134a) and pure difluoromethane (R-32) were measured over the temperature range (253 to 333) K using a differential capillary rise method (DCRM) under vapor−liquid equilibrium conditions. The temperature and surface tension uncertainties were estimated to be within ±10 mK and $\pm 0.15\ \mathrm{mN\cdot m^{-1}}$, respectively. The present data were used to develop a van der Waals-type surface tension correlation for pure R-32. Correlations for pure R-32 and R-134a were used to develop a surface tension correlation for the experimental data of the R-32 + R-134a mixtures as a function of the mass fraction.

Introduction

Because of the ozone layer depletion and global warming caused by chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants, hydrofluorocarbon (HFC) mixtures are expected to be interim and long-term replacements for HCFC refrigerants (such as chlorodifluoromethane (R-22)) and R-502. Surface tension is a basic thermophysical property, related to vapor−liquid interfacial effects that must be known to analyze the heat transfer through heat-exchanging surfaces with bubbles or fluid drops.

This paper presents surface tension measurements for pure R-32 and binary mixtures of R-32 + R-134a in the temperature range from (253 to 333) K. The experimental results for pure R-32 were represented with a van der Waals-type surface tension correlation. The experimental mixture data were then used to develop a surface tension correlation for R-32 + R-134a mixtures as a function of the mass fraction using the correlations for pure R-32 and R-134a.

Experimental Section

Mixture Preparation. The sample of pure R-32 was purchased 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 %. 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 %. A gas chromatograph with a thermal conductivity detector (TCD) and an ODPN column was used to examine the samples, and no impurities were detected.

The mixtures were gravimetrically prepared using an accurate electronic balance with a resolution of ±0.001 g. Four R-32 (1) + R-134a (2) binary mixtures were prepared at nominal mass fractions (the liquid and vapor average composition) w'_1 of 0.2379, 0.4017, 0.6235, and 0.7628.

Apparatus and Procedure. The surface tension was measured using the direct optical measurement system shown in Figure 1 based on the differential capillary rise method. The apparatus has been described in detail[1−5] and is only briefly described here. The measurement system includes a moveable coordinate frame, a telescope, and an accurate displacement sensor.

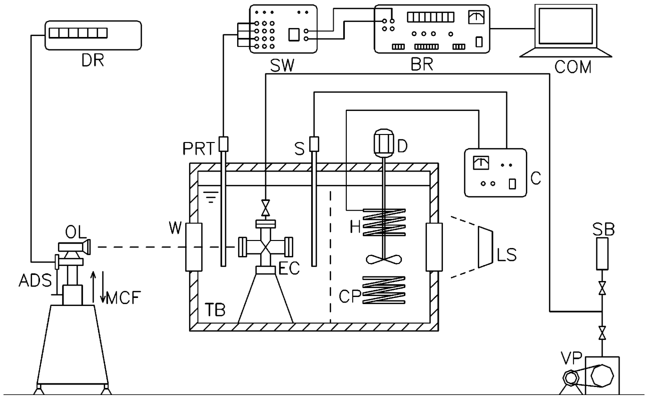

Figure 1. Surface-tension apparatus: MCF, movable coordinate frame; OL, optical level instrument; ADS, accurate displacement sensor; DR, digital readout; EC, experimental cell; TB, thermostated bath; H, heater; CP, cooling pipe; D, dynamic-electric stirrer; S, thermal-sensitive resistance sensor; C, controller; PRT, platinum resistance thermometer; SW, selector switch; BR, automatic thermometer bridge; COM, computer; W, window; LS, light source; VP, vacuum pump; SB, sample bottle.

The sample cell contained 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 sample cell was installed in a thermostated bath. The bath temperature could be varied from (233 to 453) K. The temperature instability in the bath is less than ±5 mK in 8 h. 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 tem-

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Table 1. Experimental Surface Tension Data and Capillary Constants for R-32

			a^2/mm^2		σ/mN·m^{-1}	
T/K	ρ_l/kg·m^{-3}	ρ_v/kg·m^{-3}	(3,2)	(3,1)	(3,2)	(3,1)
252.74	1121.9	10.99	2.688	2.686	14.631	14.621
257.00	1108.5	12.82	2.563	2.568	13.760	13.787
260.46	1097.4	14.47	2.480	2.484	13.160	13.182
265.04	1082.6	16.92	2.374	2.378	12.396	12.417
268.75	1070.3	19.14	2.296	2.296	11.825	11.825
273.28	1054.9	22.18	2.176	2.176	11.011	11.011
276.85	1042.4	24.85	2.097	2.102	10.455	10.480
281.50	1025.7	28.74	1.965	1.972	9.600	9.634
285.79	1009.8	32.77	1.840	1.840	8.809	8.809
294.05	977.8	41.96	1.645	1.647	7.543	7.552
297.58	963.4	46.56	1.552	1.554	6.972	6.981
301.42	947.1	52.09	1.454	1.453	6.377	6.373
305.30	930.1	58.31	1.358	1.356	5.801	5.792
309.50	910.7	65.88	1.245	1.245	5.154	5.154
315.58	880.8	78.67	1.081	1.084	4.249	4.260
319.38	860.6	88.01	0.967	0.970	3.661	3.672
319.84	858.1	89.23	0.947	0.948	3.568	3.571
323.29	838.4	98.97	0.852	0.852	3.087	3.087
327.23	814.3	111.72	0.748	0.746	2.575	2.568
332.00	781.8	130.15	0.601	0.601	1.919	1.919

Table 2. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w'_1 = 0.2379$ for R-32 (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)
255.03	1287	10.77	0.2324	2.244	2.244	14.033	14.033
256.94	1281	11.54	0.2321	2.210	2.208	13.747	13.735
258.87	1275	12.36	0.2318	2.185	2.185	13.518	13.518
260.74	1269	13.20	0.2315	2.151	2.152	13.236	13.242
263.04	1262	14.30	0.2311	2.083	2.086	12.735	12.753
264.63	1256	15.09	0.2309	2.067	2.067	12.568	12.568
266.53	1250	16.09	0.2305	2.026	2.026	12.250	12.250
268.90	1242	17.41	0.2301	1.980	1.981	11.881	11.887
271.05	1235	18.68	0.2297	1.941	1.946	11.568	11.598
273.66	1227	20.33	0.2292	1.890	1.897	11.175	11.216
278.13	1211	23.40	0.2283	1.805	1.814	10.504	10.556
282.42	1196	26.70	0.2274	1.729	1.729	9.906	9.906
286.04	1184	29.78	0.2266	1.660	1.660	9.388	9.388
288.32	1175	31.86	0.2261	1.628	1.628	9.119	9.119
292.49	1160	35.97	0.2251	1.526	1.529	8.405	8.421
295.14	1150	38.82	0.2245	1.475	1.473	8.031	8.020
296.81	1143	40.70	0.2240	1.439	1.434	7.772	7.745
298.62	1136	42.84	0.2236	1.406	1.407	7.531	7.537
300.47	1129	45.12	0.2232	1.359	1.360	7.218	7.223
302.58	1121	47.85	0.2227	1.334	1.339	7.015	7.041
304.89	1111	51.01	0.2221	1.295	1.298	6.726	6.742
306.90	1103	53.90	0.2216	1.249	1.244	6.421	6.395
308.95	1094	57.00	0.2210	1.223	1.223	6.214	6.214
310.59	1087	59.60	0.2206	1.188	1.188	5.981	5.981
311.21	1085	60.61	0.2204	1.173	1.170	5.888	5.873
313.15	1076	63.85	0.2199	1.141	1.139	5.659	5.649
315.19	1067	67.48	0.2193	1.077	1.078	5.275	5.280
317.10	1058	71.03	0.2188	1.065	1.061	5.151	5.131
318.71	1051	74.16	0.2184	1.034	1.033	4.949	4.944
319.34	1048	75.42	0.2182	1.012	1.016	4.823	4.842
321.24	1039	79.35	0.2177	0.983	0.984	4.622	4.627
323.11	1030	83.42	0.2172	0.942	0.942	4.369	4.369
325.33	1018	88.52	0.2166	0.895	0.895	4.076	4.076
327.26	1009	93.22	0.2161	0.868	0.870	3.895	3.904
329.46	996.9	98.89	0.2155	0.822	0.820	3.617	3.608
331.37	986.4	104.10	0.2150	0.780	0.778	3.372	3.364
333.53	974.3	110.40	0.2144	0.725	0.724	3.069	3.065

Table 3. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w'_1 = 0.4017$ for R-32 (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)
254.88	1246	11.63	0.3944	2.302	2.302	13.923	13.923
256.82	1240	12.47	0.3940	2.281	2.280	13.720	13.714
259.08	1233	13.50	0.3935	2.225	2.225	13.296	13.296
261.21	1226	14.54	0.3930	2.188	2.188	12.988	12.988
262.98	1220	15.44	0.3926	2.137	2.143	12.613	12.649
265.09	1213	16.58	0.3921	2.109	2.108	12.364	12.358
266.90	1207	17.61	0.3916	2.070	2.070	12.064	12.064
269.06	1200	18.91	0.3911	2.034	2.033	11.771	11.766
271.09	1193	20.20	0.3905	1.976	1.978	11.356	11.367
275.81	1177	23.47	0.3892	1.896	1.898	10.717	10.728
278.11	1170	25.21	0.3885	1.842	1.845	10.333	10.349
280.06	1163	26.76	0.3879	1.811	1.815	10.083	10.105
282.23	1155	28.59	0.3872	1.740	1.743	9.604	9.620
283.25	1151	29.48	0.3869	1.736	1.738	9.540	9.551
286.27	1141	32.26	0.3859	1.684	1.686	9.149	9.160
289.25	1130	35.21	0.3849	1.617	1.616	8.674	8.669
291.23	1122	37.30	0.3842	1.575	1.576	8.371	8.376
293.41	1114	39.72	0.3835	1.513	1.515	7.964	7.975
295.48	1106	42.14	0.3827	1.467	1.471	7.647	7.668
297.23	1099	44.28	0.3821	1.447	1.447	7.478	7.478
299.20	1091	46.81	0.3813	1.395	1.398	7.138	7.153
301.19	1083	49.49	0.3805	1.365	1.364	6.913	6.908
303.43	1074	52.67	0.3797	1.327	1.328	6.641	6.646
305.51	1066	55.78	0.3788	1.278	1.280	6.326	6.336
307.34	1058	58.66	0.3781	1.241	1.239	6.077	6.067
309.23	1050	61.77	0.3773	1.216	1.214	5.888	5.879
311.60	1039	65.90	0.3764	1.151	1.148	5.488	5.474
313.64	1030	69.65	0.3755	1.106	1.102	5.205	5.186
315.26	1023	72.78	0.3748	1.080	1.079	5.029	5.024
317.40	1012	77.12	0.3739	1.025	1.022	4.695	4.682
319.24	1004	81.06	0.3731	0.986	0.983	4.459	4.446
321.49	992.5	86.15	0.3721	0.951	0.950	4.224	4.219
323.44	982.6	90.82	0.3713	0.899	0.901	3.928	3.937
325.43	972.2	95.87	0.3704	0.863	0.862	3.706	3.701
327.18	962.9	100.60	0.3697	0.818	0.820	3.456	3.465
329.24	951.5	106.40	0.3687	0.768	0.767	3.180	3.176
331.50	938.6	113.20	0.3677	0.723	0.723	2.924	2.924

perature scale of 1990 (ITS-90). 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 differential capillary rise between two capillaries was sensed by a height transducer on the telescope using a digital readout. The contact angle, θ, was assumed to be zero, since the inner walls of the capillaries were carefully washed before the measurements.

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

The binary mixture of R-32 + R-134a in the sample cell was prepared by placing the requested amounts of R-32 and R-134a in separate gas cylinders. The two cylinders were precisely weighed on an accurate electronic balance with a resolution of ±0.001 g (Mettler Toledo PR1203). 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 requested mount of R-32 was supplied to the sample cell from the other gas cylinder using the same procedure as 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 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

Table 4. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w'_1 = 0.6235$ for R-32 (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)
254.88	1194	12.07	0.6169	2.384	2.388	13.807	13.830
257.14	1187	13.09	0.6164	2.347	2.347	13.500	13.500
258.98	1181	13.96	0.6160	2.296	2.296	13.130	13.130
261.04	1174	14.99	0.6156	2.269	2.271	12.886	12.897
263.08	1168	16.08	0.6151	2.212	2.222	12.485	12.542
264.91	1162	17.10	0.6146	2.194	2.196	12.308	12.320
266.52	1156	18.04	0.6142	2.145	2.152	11.961	12.000
268.91	1148	19.52	0.6136	2.108	2.109	11.656	11.662
270.89	1142	20.82	0.6131	2.048	2.051	11.251	11.268
273.21	1134	22.43	0.6125	2.002	2.000	10.904	10.893
274.56	1129	23.41	0.6121	1.971	1.974	10.678	10.694
277.22	1120	25.44	0.6113	1.926	1.925	10.330	10.324
279.20	1113	27.05	0.6107	1.871	1.871	9.956	9.956
282.76	1101	30.16	0.6095	1.777	1.777	9.324	9.324
287.13	1085	34.39	0.6080	1.707	1.709	8.788	8.798
289.78	1075	37.18	0.6071	1.645	1.648	8.365	8.381
291.41	1068	39.00	0.6065	1.590	1.593	8.017	8.032
293.56	1060	41.52	0.6057	1.544	1.545	7.705	7.710
295.58	1052	44.01	0.6049	1.493	1.493	7.374	7.374
297.26	1046	46.18	0.6042	1.454	1.454	7.123	7.123
299.20	1038	48.80	0.6034	1.427	1.426	6.917	6.912
301.54	1028	52.15	0.6024	1.361	1.362	6.508	6.513
303.56	1020	55.21	0.6015	1.328	1.329	6.278	6.283
305.76	1010	58.72	0.6006	1.289	1.289	6.008	6.008
307.52	1003	61.69	0.5997	1.249	1.249	5.761	5.761
309.37	994.3	64.96	0.5989	1.196	1.195	5.446	5.442
311.69	983.8	69.29	0.5978	1.137	1.137	5.095	5.095
313.91	973.4	73.70	0.5967	1.100	1.105	4.849	4.871
315.46	966.0	76.95	0.5959	1.046	1.051	4.557	4.579
317.56	955.7	81.58	0.5949	1.002	1.005	4.292	4.305
319.70	945.0	86.59	0.5937	0.960	0.957	4.038	4.025
321.73	934.5	91.65	0.5927	0.904	0.903	3.733	3.729
323.69	924.0	96.83	0.5916	0.845	0.846	3.425	3.429
325.56	913.7	102.10	0.5907	0.809	0.811	3.217	3.225
327.99	899.9	109.40	0.5893	0.761	0.760	2.948	2.944
329.50	891.0	114.20	0.5884	0.719	0.717	2.737	2.729
331.70	877.5	121.70	0.5872	0.669	0.667	2.478	2.470

Table 5. Experimental Surface Tension Data and Capillary Constants for Nominal Mass Fraction $w'_1 = 0.7628$ for R-32 (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)
254.87	1163	12.09	0.7577	2.474	2.477	13.952	13.969
257.00	1157	13.04	0.7574	2.435	2.435	13.649	13.649
258.96	1150	13.97	0.7571	2.398	2.392	13.349	13.315
261.07	1144	15.03	0.7567	2.341	2.337	12.950	12.928
262.98	1138	16.05	0.7563	2.293	2.293	12.606	12.606
264.74	1132	17.03	0.7560	2.255	2.257	12.320	12.331
267.08	1124	18.42	0.7555	2.204	2.207	11.940	11.956
268.95	1118	19.59	0.7551	2.172	2.170	11.690	11.679
270.70	1112	20.74	0.7548	2.138	2.138	11.432	11.432
273.32	1103	22.56	0.7542	2.064	2.060	10.927	10.906
275.42	1096	24.12	0.7537	2.024	2.031	10.630	10.667
276.93	1091	25.29	0.7533	1.982	1.982	10.350	10.350
279.23	1083	27.17	0.7527	1.933	1.924	10.001	9.954
281.69	1074	29.30	0.7521	1.871	1.876	9.578	9.603
283.16	1068	30.65	0.7517	1.831	1.837	9.307	9.337
285.86	1058	33.25	0.7509	1.778	1.776	8.928	8.918
289.77	1044	37.36	0.7498	1.680	1.682	8.287	8.297
291.86	1036	39.73	0.7491	1.634	1.634	7.977	7.977
293.49	1029	41.68	0.7486	1.569	1.568	7.591	7.586
295.30	1022	43.93	0.7480	1.560	1.560	7.476	7.476
297.55	1013	46.89	0.7472	1.478	1.477	6.997	6.992
299.27	1006	49.27	0.7466	1.465	1.464	6.868	6.863
301.42	997.3	52.40	0.7458	1.407	1.408	6.514	6.519
303.42	988.8	55.48	0.7451	1.357	1.359	6.206	6.215
305.51	979.7	58.87	0.7443	1.302	1.304	5.875	5.884
307.72	969.9	62.68	0.7434	1.250	1.250	5.557	5.557
309.65	961.2	66.20	0.7426	1.212	1.210	5.315	5.306
311.59	952.2	69.94	0.7417	1.161	1.162	5.019	5.023
313.99	940.8	74.85	0.7407	1.102	1.100	4.676	4.667
315.42	933.8	77.95	0.7401	1.067	1.067	4.475	4.475
317.42	923.8	82.50	0.7392	1.016	1.016	4.188	4.188
319.64	912.4	87.88	0.7381	0.961	0.961	3.883	3.883
321.58	902.1	92.90	0.7372	0.902	0.901	3.577	3.573
323.49	891.6	98.15	0.7362	0.859	0.860	3.340	3.344
325.54	880.0	104.20	0.7352	0.815	0.815	3.098	3.098
327.40	869.1	110.00	0.7343	0.771	0.771	2.868	2.868
329.68	855.1	117.70	0.7331	0.705	0.708	2.547	2.558
331.97	840.4	126.10	0.7318	0.645	0.646	2.258	2.261
333.49	830.1	132.10	0.7310	0.609	0.611	2.083	2.090

Table 6. Numerical Constants in Eq 4 for R-32

refrigerant	σ_0/mN·m^{-1}	n	T_c/K
R-32	68.936	1.220	351.255[9]

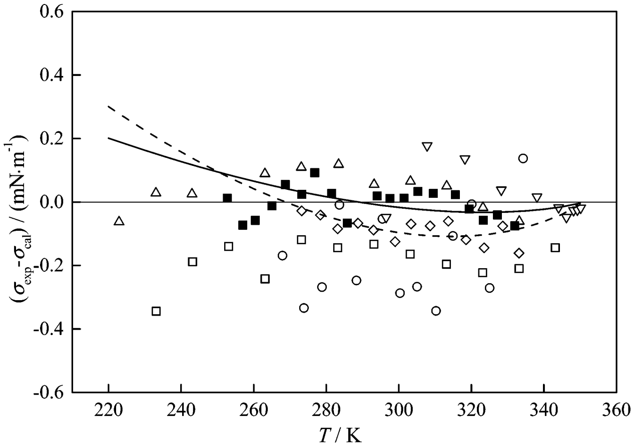

Figure 2. Absolute deviations of experimental surface tension data from eq 4 for R-32: ■, present work; ○, Zhu;[2] △, Heide;[11] ▽, Schmidt;[12] ◇, Okada;[13] □, Fröba;[14] —, Heide;[11] - - -, Okada.[13]

mass fraction uncertainty was estimated to be better than ±0.01 mass %.

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-32 (1) + R-134a (2) mixture at the four nominal mass fractions w'_1 of 0.2379, 0.4017, 0.6235, and 0.7628 is azeotropic, so the coexisting liquid and vapor compositions differed. The compositions were determined by measuring the liquid phase volume in the sample cell, based on the liquid height in the cell. The saturated liquid and vapor densities were calculated using NIST REFPROP 6.01.[6] The actual liquid phase composition was then calculated from the volumes and densities of the liquid and vapor phases in the sample cell. To verify the results, the gas phase composition was checked using a gas chromatograph (Lunan SP-6800A) with a thermal conductivity detector (TCD) and an ODPN column 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 ±0.002.

Results and Discussion

The capillary constant is

$$a^2 = 2\sigma/(\rho_l - \rho_v)g \tag{1}$$

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[6] for the refrigerant mixture R-32 + R-134a and from available literature data for R-32.[7]

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

Table 7. Coefficient in Eq 5 and Absolute and Relative Deviations between Experimental and Calculated Values

mixture	C	$\overline{\delta_a}^a$/mN·m^{-1}	$\overline{\delta_r}^a$/%
R-32 + R-134a	−1.2773	0.039	0.59

$\overline{\delta_a} = 1/n\sum_{i=1}^{n}|\sigma_{\text{exp},i} - \sigma_{\text{cal},i}|$; $\overline{\delta_r} = 1/n\sum_{i=1}^{n}|\sigma_{\text{exp},i} - \sigma_{\text{cal},i}|/\sigma_{\text{cal},i}$.

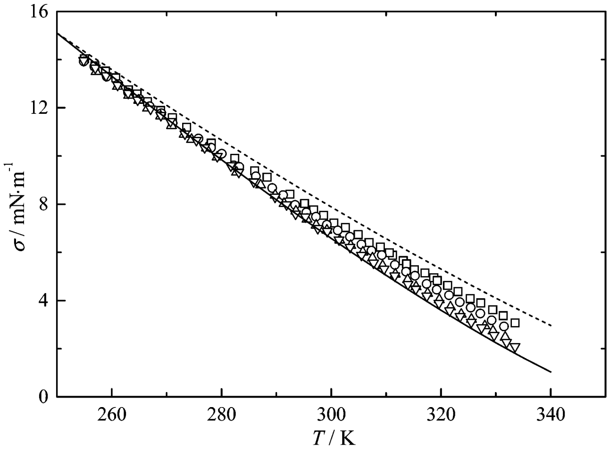

Figure 3. Surface tension vs temperature of R-32 (1) + R-134a (2): □, $w_1' = 0.2379$; ○, $w_1' = 0.4017$; △, $w_1' = 0.6235$; ▽, $w_1' = 0.7628$; —, R-134a;[10] - - -, R-32.

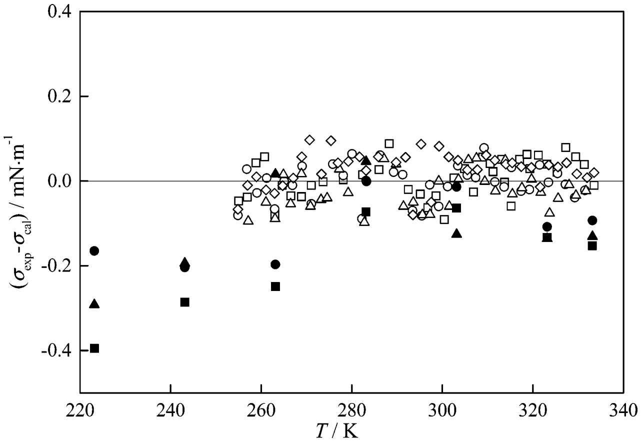

Figure 4. Absolute deviations of experimental surface tension data of R-32 (1) + R-134a (2) from eq 5: □, $w_1' = 0.2379$; ○, $w_1' = 0.4017$; △, $w_1' = 0.6235$; ◇, $w_1' = 0.7628$; ■, $w_1' = 0.228$, Heide;[11] ●, $w_1' = 0.477$, Heide;[11] ▲, $w_1' = 0.718$, Heide.[11]

calculated using Rayleigh's correlation.[8] The capillary constant can be related to the rise heights as

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

Therefore, the surface tension can be calculate from

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

Using the differential capillary rise method (DCRM) based on the height difference between two different capillaries, 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 reported in Table 1 for R-32 and in Tables 2−5 for R-32 + R-134a mixtures. The saturated liquid density, ρ_l, the saturated vapor density, ρ_v, and the capillary constant, a^2, are also listed in Tables 1−5. The liquid mass fraction of R-32 (w_1) in the mixtures at each temperature is also listed in Tables 2−5.

The surface tension is normally correlated as a function of temperature for pure refrigerants by a van der Waals-type correlation:

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

where σ_0 and n are empirical constants obtained from a least-squares fit of the experimental data. The value of n normally falls between 1.2 and 1.3 for most fluids. The data in Table 1 were used to calculate the values of σ_0 and n for R-32 listed in Table 6, and the critical temperature of R-32 was 351.255 K.[9] The values of σ_0 and n for R-134a were assumed to be 60.74 and 1.262, and the critical temperature of R-134a was taken as 374.21 K.[10] Figure 2 shows the absolute deviations between eq 4 with the constants listed in Table 6 and the present measurements and other experimental data[2,11−14] for R-32. The plot shows that the present results are scattered within ±0.15 mN·m^{-1}, which is consistent with the estimated uncertainty. The present data and eq 4 also agree with the correlations of Okada[13] and Heide[11] within ±0.2 mN·m^{-1}.

The surface tension correlation used for the R-32 + R-134a mixtures was[11]

$$\sigma = w_1\sigma_1 + w_2\sigma_2 + w_1w_2C \tag{5}$$

where σ_1 and σ_2 are the surface tensions of the pure refrigerants calculated using eq 4 and w_1 and w_2 are the mass fractions. The coefficient C was determined by fitting eq 5 to the present experimental data. Table 7 lists the values of C, the average absolute deviation, and the average relative deviation of the present experimental data from eq 5. Figure 3 shows the surface tension variation for the R-32 + R-134a mixtures, pure R-32, and pure R-134a as a function of temperature. Figure 4 shows the absolute deviations of the present data and other experimental data from eq 5 for R-32 + R-134a mixtures with various mass fractions. The results in Figure 4 show that the absolute deviations of the present data from eq 5 are less than ±0.15 mN·m^{-1}. Heide's[11] measurements agree well with the present results for temperatures above 280 K, but his data are (0.2 to 0.4) mN·m^{-1} lower than those of eq 5 for the temperature range from (223 to 263) K, with corresponding relative deviations of (1 to 2)%.

Conclusions

The surface tensions of the binary mixture R-32 + R-134a and pure R-32 were measured over a wide temperature range using a differential capillary rise method at four nominal mass fractions. The uncertainty of the surface tension measurements was estimated to be within ±0.15 mN·m^{-1}. The experimental data were then used to develop correlations for the surface tensions of pure R-32 and of the binary mixture R-32 + R-134a.

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