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Surface Tension of Ternary Mixtures of Nitrogen, Oxygen, and Argon

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Surface tensions for the liquid mixture nitrogen + oxygen + argon have been measured using the capillary rise method. The measurements were made for various compositions at temperatures from 90 to 115 K and at vapor pressures up to 900 kPa. The experimental data were correlated with those calculated from a simple equation using the pure component results.

Introduction

The surface tension of liquid nitrogen, oxygen, and argon is an important property in designing a distillation column for an oxygen plant. Although measurements have been carried out for the pure components (*1–3*), few measurements have been made on the binary and none on the ternary mixtures. In the present study, we report the surface tensions of the liquid mixture nitrogen + oxygen + argon. The results were correlated using a simple equation containing an adjustable parameter.

Experimental Section

The differential capillary rise method was used. Figure 1 illustrates the experimental apparatus. Four capillary tubes of different bore size were fixed to a supporting rod. The bore size was obtained from the measurements of the length and weight of mercury enclosed in the capillary before the experiments. The measurements were carried out at some positions along the axis of the capillary. We checked the variation in bore size along the axis of the capillary and selected four capillary tubes of uniform bore from about thirty tubes tested. The bore sizes of the capillaries were 0.1827, 0.2504, 0.3061, and 0.4249 mm. The variation in the bore size over the working length was estimated to be ±0.4% for each capillary. The capillaries were cleaned with hot chromic acid, water, and acetone before use.

The supporting rod was placed in a cylindrical pressure cell made of stainless steel. Two glass windows in the cell wall allowed illumination and observation of the interior of the cell. The cell containing synthetic liquid air was cooled by passing liquid nitrogen through an outer jacket. The cell was fixed in a cold box made of aluminum plates and acrylic resin plates. Small Styrofoam balls were stuffed into the cold box as heat insulating materials.

The synthetic liquid air was composed of nitrogen, oxygen, and argon. The impurity was below 4 ppm according to the supplier (Nippon Sanso Co., Ltd.). Before an experimental run, the whole gas system was evacuated and flushed with nitrogen gas. The liquid mixture was introduced into the cell, and the liquid surface was adjusted to be observable from the windows. The pressure in the cell was controlled by valves and measured using a pressure transducer with a precision of ±0.11%. Temperature was kept constant by maintaining a constant pressure. The temperatures of the vapor phase and the liquid phase were measured with digital thermometers with an accuracy of ±0.15 K. When the pressure and temperature stabilized, the system was considered to have reached thermal and mass transfer equilibrium. It took about 20 min to reach the equilibrium. At this time, photographs were taken and a small amount of liquid was sampled. The mixture sampled was vaporized and analyzed using a gas chromatograph. The absolute error in the composition expressed in mole fraction was estimated to be less than 0.005.

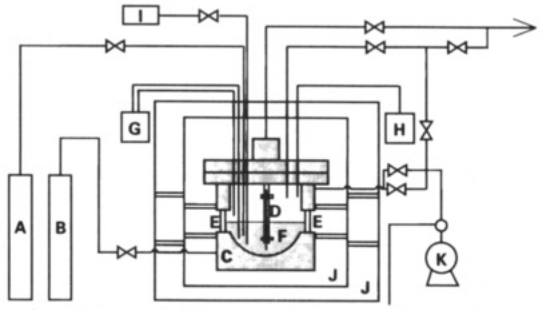

Figure 1. Schematic diagram of the experimental setup used to measure the surface tension of synthetic liquid air: (A) liquid synthetic air, (B) liquid nitrogen, (C) cell, (D) capillaries, (E) windows, (F) fluid measured, (G) temperature measuring unit, (H) pressure measuring unit, (I) gas chromatograph, (J) cold boxes, (K) vacuum pump.

Table 1. Parameters in Eq 3

system	σ_0/(mN m^{-1})	p	dev^a/%
nitrogen	28.2	1.235	0.90
oxygen	39.5	1.255	0.99
argon	38.7	1.299	1.09

[a] Average deviation = $\sum(\sigma(\mathrm{exp}) - \sigma(\mathrm{calc}))/\sigma(\mathrm{exp})$.

The pressure in the cell was then raised to the next desired value, and another set of measurements was made. The procedure outlined above was repeated. In the present study, the measurements were carried out over a pressure range between 260 and 900 kPa judging from the condition of industrial distillation columns.

The difference in the height between the points of the menisci of two capillaries was obtained from the photograph using a caliper rule. The value of the capillary constant was calculated from the equation

$$a^2 = \Delta h/(1/b_1 - 1/b_2) \tag{1}$$

where b_1 and b_2 are the radii of curvature at the bottom of the two menisci. Because the relationship between the radii of curvature and the capillary constant is given in Sugden's table (*4*), the value of the capillary constant was obtained by iteration. The values obtained from the six combinations of the four capillaries for one condition were averaged. Finally, the surface tension was calculated by

$$\sigma = a^2 g(\rho_L - \rho_V)/2 \tag{2}$$

where g is the acceleration due to gravity and ρ_L and ρ_V are

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Table 2. Surface Tension for the N_2 (1) + O_2 (2) + Ar (3) Ternary System

T/K	P/kPa	x_1	x_2	σ/(mN m^{-1})	T/K	P/kPa	x_1	x_2	σ/(nM m^{-1})	T/K	P/kPa	x_1	x_2	σ/(mN m^{-1})
90.1	262.0	0.080	0.505	8.61	98.4	391.5	0.096	0.722	8.62	104.7	485.5	0.361	0.494	8.41
91.1	265.0	0.078	0.506	8.41	98.4	419.5	0.096	0.722	7.91	104.9	734.9	0.357	0.496	6.01
92.3	303.0	0.077	0.507	7.97	98.5	390.8	0.092	0.725	8.75	105.2	500.7	0.359	0.495	8.29
93.5	311.8	0.076	0.509	8.52	98.5	467.0	0.089	0.728	7.62	105.2	523.5	0.357	0.497	7.70
93.6	348.0	0.075	0.509	7.95	98.6	425.4	0.184	0.782	7.94	105.8	510.0	0.358	0.495	8.36
93.8	263.7	0.107	0.476	9.91	98.6	443.4	0.184	0.782	8.08	105.6	510.5	0.355	0.499	8.09
93.9	342.9	0.073	0.511	8.30	98.6	501.8	0.186	0.781	7.09	105.7	521.1	0.356	0.398	8.12
94.1	328.2	0.160	0.577	8.34	98.6	399.4	0.178	0.788	8.23	105.7	532.5	0.357	0.497	8.02
94.2	355.0	0.154	0.583	7.76	98.7	440.5	0.181	0.785	8.12	105.9	556.2	0.352	0.501	7.53
94.4	337.6	0.156	0.586	8.27	98.7	509.6	0.178	0.788	6.84	105.9	635.7	0.292	0.661	6.88
94.6	239.9	0.153	0.583	10.24	98.7	394.4	0.178	0.788	8.37	106.0	550.5	0.265	0.688	7.75
94.6	380.1	0.142	0.595	7.85	98.7	312.0	0.175	0.791	9.12	106.1	650.3	0.265	0.690	6.97
94.7	248.8	0.144	0.593	9.76	98.7	564.0	0.170	0.795	6.47	106.3	534.0	0.259	0.695	7.77
94.7	243.8	0.134	0.602	10.07	98.8	432.5	0.171	0.796	7.95	106.4	563.9	0.263	0.691	7.56
94.7	335.5	0.133	0.602	8.03	99.0	439.4	0.167	0.799	8.03	106.5	577.2	0.289	0.667	7.62
94.8	362.9	0.134	0.602	8.02	99.1	520.2	0.167	0.798	6.70	106.6	796.3	0.250	0.704	6.00
94.8	346.9	0.143	0.592	8.14	99.2	412.3	0.130	0.831	8.44	106.7	591.8	0.285	0.670	7.51
95.0	373.7	0.142	0.593	7.51	99.2	446.7	0.127	0.834	7.95	106.7	582.5	0.283	0.670	7.29
95.0	351.8	0.138	0.596	8.23	99.5	314.6	0.104	0.856	9.83	106.8	588.6	0.172	0.551	7.25
95.0	252.2	0.143	0.593	9.99	99.6	465.3	0.107	0.852	7.88	106.9	586.8	0.191	0.530	7.44
95.1	257.4	0.106	0.626	9.95	99.7	339.6	0.102	0.857	9.53	107.0	518.1	0.190	0.531	8.08
95.1	350.4	0.104	0.624	8.04	99.9	327.4	0.101	0.858	9.67	107.0	720.3	0.185	0.536	6.56
95.3	362.6	0.118	0.549	8.15	100.0	495.9	0.099	0.860	7.77	107.0	605.1	0.180	0.542	7.29
95.3	261.8	0.124	0.542	9.78	100.2	484.5	0.093	0.866	7.83	107.1	593.6	0.181	0.540	7.56
95.5	214.6	0.116	0.549	10.44	100.3	354.4	0.097	0.858	8.80	107.3	572.8	0.188	0.533	7.71
95.5	362.6	0.096	0.569	7.91	100.3	452.7	0.070	0.842	8.25	107.4	615.9	0.198	0.527	7.25
95.6	305.7	0.094	0.571	9.19	100.4	497.4	0.073	0.884	7.67	107.4	603.2	0.196	0.528	7.54
95.6	372.9	0.096	0.568	8.07	100.4	329.7	0.071	0.886	9.71	107.6	627.0	0.187	0.535	7.23
95.6	266.8	0.099	0.565	9.80	100.4	482.4	0.073	0.883	7.83	107.7	626.6	0.195	0.528	7.41
95.7	363.5	0.097	0.568	7.97	100.4	493.1	0.076	0.881	7.84	107.7	598.2	0.180	0.545	7.45
95.7	365.2	0.117	0.549	7.87	100.5	360.4	0.074	0.882	9.36	107.8	603.5	0.177	0.545	7.42
95.8	369.7	0.098	0.566	7.94	100.7	339.9	0.073	0.883	9.48	107.8	746.0	0.412	0.365	6.43
95.9	368.2	0.099	0.565	7.98	100.7	370.0	0.073	0.884	9.10	107.9	637.3	0.394	0.377	7.76
95.9	315.8	0.097	0.567	8.85	100.9	346.4	0.069	0.886	9.28	108.0	614.2	0.410	0.367	7.49
95.9	379.7	0.088	0.577	8.11	101.1	379.9	0.068	0.889	9.19	108.1	648.9	0.401	0.375	7.09
96.0	345.5	0.087	0.592	8.24	101.1	351.8	0.293	0.496	9.27	108.1	649.3	0.404	0.371	7.32
96.0	371.5	0.090	0.588	7.96	101.2	357.5	0.280	0.508	9.03	108.2	559.7	0.563	0.356	7.67
96.0	272.5	0.092	0.585	9.72	101.3	389.9	0.276	0.512	8.92	108.4	610.9	0.596	0.327	7.67
96.0	425.3	0.084	0.594	7.33	101.5	367.2	0.284	0.503	9.05	108.4	629.3	0.561	0.358	7.89
96.1	275.9	0.078	0.602	9.57	101.6	362.4	0.289	0.425	9.25	108.5	667.1	0.553	0.366	6.93
96.1	386.9	0.196	0.671	7.91	101.6	399.9	0.273	0.438	8.82	108.6	663.1	0.559	0.358	7.37
96.2	281.5	0.191	0.675	9.67	101.7	399.3	0.279	0.433	8.64	108.9	584.8	0.556	0.363	7.59
96.2	391.9	0.151	0.672	8.07	101.7	371.7	0.330	0.391	9.08	108.9	681.8	0.543	0.375	7.04
96.2	278.8	0.149	0.674	9.64	101.8	407.6	0.329	0.400	8.98	109.0	680.0	0.457	0.362	7.23
96.2	436.7	0.148	0.674	7.33	101.8	617.2	0.315	0.411	6.77	109.0	652.7	0.452	0.368	7.06
96.3	322.0	0.147	0.675	8.45	101.9	413.7	0.332	0.397	9.10	109.1	686.8	0.451	0.368	7.05
96.4	331.5	0.146	0.677	8.63	102.0	501.0	0.330	0.401	7.31	109.1	686.8	0.452	0.369	7.02
96.4	285.2	0.144	0.679	9.75	102.0	379.1	0.335	0.395	9.16	109.3	700.5	0.454	0.366	7.25
96.5	379.1	0.120	0.699	8.20	102.1	385.3	0.438	0.455	8.90	109.3	728.5	0.449	0.372	6.92
96.5	452.0	0.120	0.700	7.15	102.2	421.0	0.349	0.536	8.77	109.4	602.8	0.452	0.372	7.53
96.7	229.9	0.116	0.704	10.87	102.3	429.4	0.439	0.453	8.83	109.6	809.9	0.452	0.369	6.09
96.7	341.4	0.147	0.670	8.56	102.3	391.9	0.401	0.488	8.84	109.6	772.2	0.452	0.369	6.58
96.7	384.6	0.146	0.670	8.16	102.4	400.0	0.268	0.391	8.91	109.6	737.3	0.450	0.369	6.94
96.9	231.0	0.145	0.670	10.59	102.6	404.8	0.268	0.391	8.44	109.7	616.7	0.415	0.391	7.40
96.9	396.7	0.109	0.703	7.92	102.6	436.6	0.266	0.392	8.67	109.8	748.1	0.423	0.382	6.51
96.9	478.8	0.155	0.685	6.72	102.7	410.4	0.270	0.388	8.55	110.0	865.0	0.422	0.388	6.05
97.0	291.6	0.165	0.671	9.91	102.8	415.5	0.270	0.388	8.66	110.0	753.5	0.427	0.384	6.73
97.0	391.2	0.165	0.672	7.92	102.9	634.3	0.273	0.386	6.58	110.1	730.8	0.520	0.415	6.68
97.1	502.5	0.162	0.674	6.90	102.9	448.9	0.272	0.388	8.60	110.2	631.9	0.535	0.402	7.37
97.3	356.9	0.159	0.676	8.53	103.0	552.7	0.262	0.394	7.47	110.6	813.3	0.529	0.407	6.73
97.5	268.8	0.158	0.678	9.80	103.0	385.9	0.269	0.389	9.20	110.6	648.5	0.531	0.404	7.36
97.5	399.9	0.153	0.682	8.09	103.1	642.9	0.267	0.392	6.32	110.6	776.5	0.514	0.423	6.55
97.5	351.0	0.150	0.684	8.58	103.1	560.6	0.268	0.391	7.77	110.7	780.0	0.520	0.417	6.98
97.5	418.7	0.154	0.680	8.11	103.1	419.2	0.267	0.391	8.45	111.0	920.3	0.534	0.404	5.65
97.5	478.0	0.146	0.689	7.40	103.3	656.9	0.269	0.390	6.56	111.3	748.5	0.528	0.410	7.35
97.6	366.3	0.166	0.661	8.76	103.4	435.6	0.268	0.390	8.55	111.5	799.0	0.453	0.386	6.53
97.7	404.7	0.170	0.656	8.12	103.5	530.4	0.264	0.391	7.61	111.9	788.2	0.444	0.393	6.62
97.7	448.9	0.156	0.670	7.94	103.8	588.7	0.406	0.524	7.35	112.3	810.0	0.443	0.394	6.67
97.8	428.3	0.103	0.713	7.89	104.1	475.2	0.398	0.531	8.40	112.5	824.5	0.436	0.402	6.42
97.9	409.4	0.116	0.700	7.95	104.2	498.0	0.421	0.510	7.81	112.8	850.7	0.443	0.395	6.66
97.9	453.1	0.109	0.708	8.04	104.2	599.0	0.400	0.532	6.98	112.8	842.5	0.441	0.399	6.37
97.9	533.4	0.151	0.666	6.49	104.3	466.0	0.423	0.510	8.56	113.1	861.5	0.480	0.467	6.34
98.0	439.9	0.106	0.711	7.74	104.4	500.8	0.377	0.555	7.77	113.6	852.2	0.552	0.398	6.48
98.0	461.2	0.102	0.716	7.76	104.4	490.7	0.360	0.493	8.30	113.7	854.5	0.537	0.414	6.63
98.1	542.0	0.096	0.722	6.87	104.6	707.1	0.355	0.499	6.20	113.7	853.3	0.546	0.403	6.48
98.1	412.5	0.101	0.717	8.14	104.6	480.5	0.359	0.495	8.31	113.9	857.7	0.541	0.409	6.46
98.2	417.2	0.103	0.715	7.93	104.7	620.7	0.359	0.494	6.81	114.2	877.0	0.545	0.406	6.31
98.3	528.7	0.091	0.726	7.10	104.7	580.0	0.359	0.495	7.25	114.8	904.1	0.527	0.424	6.15
98.3	374.3	0.103	0.713	8.23										

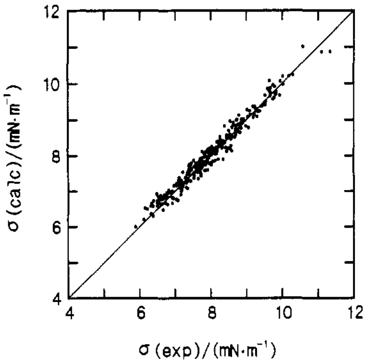

Figure 2. Comparison between measured and calculated surface tensions.

the densities of the liquid and vapor, respectively. The value of g used for the calculation was 9.7947 m·s^{-2}. The maximum error introduced by the measurement of the heights upon the obtained surface tension was estimated to be less than 1.2%.

Results and Discussion

The surface tension σ of a pure liquid can be correlated using the following equation (*5*):

$$\sigma = \sigma_0(1 - T/T_c)^p \qquad (3)$$

where T_c is the critical temperature. The values of the parameters σ_0 and p were determined from the experimental results by a least-squares analysis, and are given in Table 1. Values of p were reported to be close to 1.222 (*5*), and similar results were obtained in this study. The deviations were about 1% for the three pure components.

The experimental results for the ternary mixture are presented in Table 2. The temperature scale was the international temperature scale ITS-90. Figure 2 shows the comparison of the experimental results with the predictions from the empirical equation

$$\sigma_m{}^r = \sum_{i=1}^{3} x_i \sigma_i{}^r \qquad (4)$$

When the adjustable parameter r was 0.25, the average deviation was the smallest. The average deviation was 2.0%, and the standard deviation was 0.161 mN m^{-1}, whereas the average deviation was 5.26% and the standard deviation was 0.391 mN m^{-1} for the simple mole fraction average calculated from eq 4 in the case of $r = 1$.

Figure 3 shows the surface tension deviation at 100 K defined as

$$\delta\sigma = \sigma_m - \sigma_a \qquad (5)$$

where σ_a is the mole fraction averaged value. The value of σ_m was calculated from eq 4. The surface tension of the binary system oxygen + argon can be predicted from the simple mole fraction average with an absolute error of less than 0.1 mN m^{-1}. For the ternary mixture, however, the simple mole fraction average is not appropriate. The value of the surface tension shifts to a value smaller than the mole fraction average, especially in the case where the mole fraction of nitrogen is from 0.3 to 0.7.

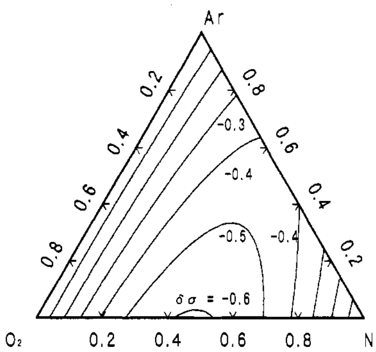

Figure 3. Relationship between the surface tension deviation and the composition of the mixture at 100 K.

Glossary

a	capillary constant
b_1, b_2	radii of curvature at the bottom of the menisci
g	acceleration due to gravity
Δh	difference in height
M_i	molecular weight
p	adjustable parameter in eq 3
r	adjustable parameter in eq 4
T	temperature
T_c	critical temperature
x_i	mole fraction

Greek Letters

$\delta\sigma$	surface tension deviation
ρ_L	density of the liquid
ρ_V	density of the vapor
σ	surface tension
σ_0	adjustable parameter in eq 3
σ_a	mole fraction average of surface tension
σ_m	surface tension of the mixture

Registry Numbers Supplied by Author. N_2, 7727-37-9; O_2, 7782-44-7; Ar, 7440-37-1.

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