

MEASUREMENT AND PREDICTION OF THE SURFACE TENSION OF NITROGEN + OXYGEN AND NITROGEN + OXYGEN + ARGON SYSTEM

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Introduction

The surface tension of liquid air is an important property for the optimum designing of distillation columns used in oxygen plants. Although the surface tensions of pure nitrogen, oxygen and argon have been reported in the literature^{1, 7, 9)}, only limited data are available for the in mixtures^{2, 3, 8)}.

In addition, it is not clear which estimation methods are the most useful for predicting the surface tension of liquid air. Many correlations have been suggested⁶⁾ for liquid mixtures of organic compounds but the application to a liquid air system is uncertain.

In the present study, the differential capillary rise method has been used to measure the surface tension for a nitrogen + oxygen binary system and for a nitrogen + oxygen + argon ternary system at low temperatures. Several correlations have been tested against the mixture data.

1. Experimental

Surface tension measurements were performed in a

cylindrical pressure vessel made of stainless steel. The diagram of the pressure vessel is shown in **Fig.1**. The vessel was cooled by passing liquid nitrogen through a jacket. Four glass capillaries were held in the vessel by a supporting rod. The inner diameters of the capillaries were 0.183, 0.250, 0.304 and 0.425 mm. The capillary assembly was illuminated through the window and was photographed by a camera through a window positioned on the other side.

The synthetic liquid air was prepared from liquid nitrogen, oxygen and argon supplied from Nippon Sanso Co., Ltd. The purity of these liquids is listed in **Table 1**. Pressure in the vapor phase was controlled by valves and the level of the liquid surface was adjusted to facilitate observation and measurement. After the vapor pressure stabilized, the capillary assembly was photographed. The pressure and temperature in the vessel were then measured. The pressure was measured using a pressure transducer with a precision of $\pm 0.11\%$. The temperature was measured with a digital thermometer with an accuracy of ± 0.15 K. The surface tension was measured at temperatures from 83 to 115 K. A sample of liquid was removed through a nozzle inserted into the vessel and the compo-

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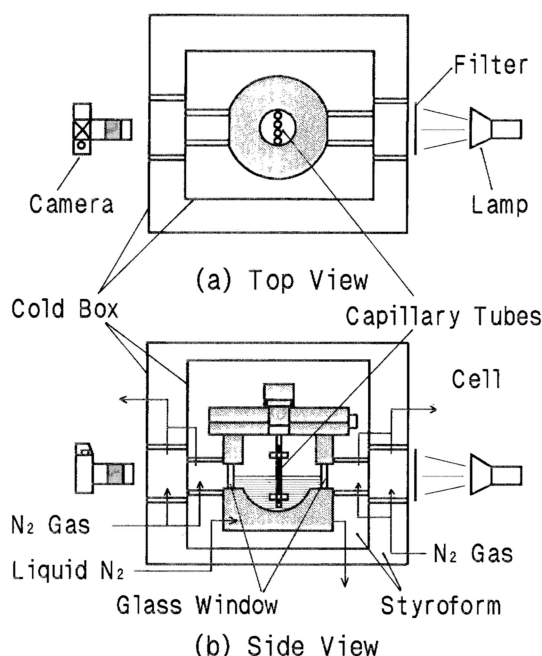


Fig. 1 Schematic drawing of cell and cold box
(a) Top view sketch, (b) Side view sketch

sition of the sample was determined by gas chromatography.

The capillary constant was calculated from the observed heights. The heights could be measured for the four capillaries so there were six independent determinations of the constant at each measurement. The surface tension was calculated using the average value of the capillary constant. The details for the experimental equipment and the procedure are given elsewhere⁵⁾.

2. Models for Prediction

Several correlations for predicting the surface tension of a liquid mixture have been proposed in the literature. The surface tension of a mixture is usually less than that calculated from a mole-fraction average of the surface tension of the pure components. Therefore, a simple mole-fraction average is of no practical use. The Macleod-Sugden correlation, corresponding-states correlation and thermodynamic correlation were tested in addition to the model proposed in this study. Details of previously proposed models are described by Reid *et al.*⁶⁾ None of the models tested in this study involve any adjustable parameters.

In the thermodynamic model, a change in chemical potential of component i is given⁸⁾ by $\mu_{MSi} - \mu_{MBi} = \sigma_{Mi} \bar{A}_i$, where μ_{MSi} and μ_{MBi} are the chemical potentials of component i in the surface and bulk phases, σ_{Mi} is the surface tension of the mixture and \bar{A}_i is the partial molar surface area of component i in the mixture. By considering the change in the chemical potential, the following equation was obtained⁸⁾:

$$\sigma_{Mi} = \frac{A_i}{A_i} \sigma_i + \frac{RT}{A_i} \ln \left(\frac{a_{Si}}{a_{Bi}} \right) \quad (1)$$

Table 1. Purity of each component

Component	Purity	Impurity
Nitrogen	99.9999 %	1 ppm (Oxygen)
Oxygen	99.8 %	0.2 % (Nitrogen + Argon)
Argon	99.999 %	5 ppm (Nitrogen) 1 ppm (Oxygen)

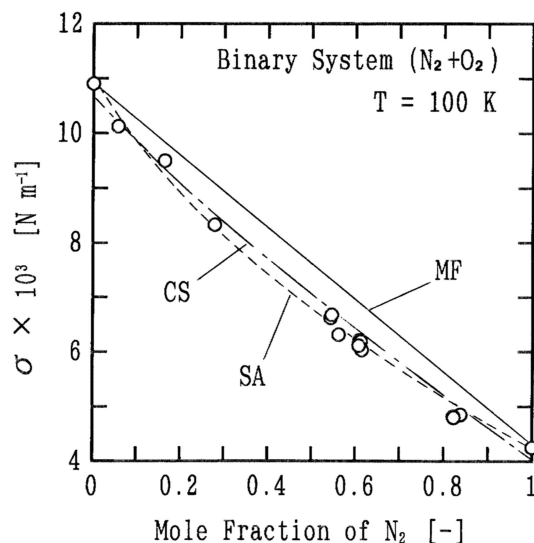


Fig. 2 Influence of mole fraction of nitrogen on mixture surface tension
MF: mole-fraction average; CS: corresponding state correlation; SA: surface area fraction average

The surface tension of component i in the mixture, σ_{Mi} , is assumed to be the same for all components in the thermodynamic model. We considered that the value of σ_{Mi} differed according to the species. Because the surface tension is the free energy based on the surface area, the surface tension of the mixture was represented by the surface area fraction average of σ_{Mi} . By assuming that the activity of the surface phase, a_{Si} is the same as that of the bulk phase, a_{Bi} , we obtain:

$$\sigma_M = \sum_{i=1}^n \theta_i \sigma_i \quad (2)$$

where θ_i is the surface area fraction of component i .

Because the fraction of the surface area is equal to the volume fraction in the bulk phase, θ_i is equal to $x_i v_i / (\sum (x_i v_i) + v_E)$. The molar volume of component i , v_i , is obtained by M_i / ρ_i , therefore the surface tension of the mixture is calculated from

$$\sigma_M = \frac{\sum_{i=1}^n x_i (M_i / \rho_i) \sigma_i}{\sum_{i=1}^n (x_i M_i) / \rho_M} \quad (3)$$

The density of the mixture, ρ_M , was calculated using a method suggested by Thomson *et al.*^{4, 10)}

3. Results and Discussion

Figure 2 shows the surface tension of a nitrogen + oxygen binary system at 100 K. The straight line in the

Table 2. Relative deviation of the calculated values from the experimental values

System	MF ¹⁾ [%]	MS ²⁾ [%]	CS ³⁾ [%]	TD ⁴⁾ [%]	SA ⁵⁾ [%]
Binary	7.34	2.30	2.28	4.02	1.85
Ternary	5.31	5.34	2.36	3.69	2.09

1)MF:mole-fraction average; 2)MS:Macleod-Sugden correlation; 3)CS:corresponding state correlation; 4)TD:thermodynamic model; 5)SA:surface area fraction average

figure shows the calculation from the mole-fraction average. It can clearly be seen that the calculated values are larger than the experimental values.

The relative deviation was determined by dividing the absolute value of the difference between the experimental and calculated values by the experimental value obtained in this study. **Table 2** summarizes the relative deviations calculated from the models mentioned in the previous section. Model SA in Table 2 was the model presented in this study. The data numbers are 362 and 235 for the binary and ternary systems, respectively. The data in the ternary system have been presented elsewhere⁵⁾.

The prediction using the mole-fraction average was the worst among all predictions. The predictions overestimated the surface tension. In the case of the Macleod-Sugden correlation, we calculated the value of the parameter called parachor from the surface tension of the pure component. This model gave a good correlation for the binary system but the results for the ternary system were not good. The deviation increased with increasing mole fraction of argon. The calculated value increased as the difference between the densities of the two components increased. It was indicated that the extension of the Macleod-Sugden correlation to liquid mixtures is limited to a system in which the difference between the densities is small.

In the case of the correlation by the corresponding state principle, the deviation was small both for the binary and ternary systems. The corresponding state correlation does not need the surface tension data of pure components. Therefore, this method is useful for a system in which the surface tension of the pure components is uncertain. However, as shown in Fig.2, this model has a disadvantage over the other model at the extremes of composition.

When the data were correlated by the equation based on the thermodynamic model, the predictions underestimated the surface tension. We also calculated the mole fraction of each component in the surface phase from this

model. The results show that the composition in the surface phase is far from that in the bulk phase and was similar to that in the vapor phase, which is in equilibrium with the bulk liquid phase.

In the case of the surface area fraction average, good correlation was obtained for the binary and ternary systems. Because the surface tension of argon is a little lower than that of oxygen, when the mole fraction of argon was low in the ternary system, the results were similar to that for the binary system. When the mole fraction of argon was larger than 30 %, it was shown that the deviation was 2.04 % and a good correlation was also obtained with the model proposed in the present study. This model is simple and it is considered to be applicable to a nonpolar system such as liquid air.

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Nomenclature

a	= activity	[-]
A	= partial molar surface area	[m ² ·mol ⁻¹]
g	= gravitational acceleration	[m·s ⁻²]
M	= molecular weight	[kg·mol ⁻¹]
R	= gas constant	[J·mol ⁻¹ ·K ⁻¹]
T	= temperature	[K]
v	= liquid molar volume	[m ³ ·mol ⁻¹]
v_E	= excess molar volume	[m ³ ·mol ⁻¹]
x	= liquid mole fraction	[-]
θ	= surface area fraction	[-]
ρ	= density	[kg·m ⁻³]
σ	= surface tension	[N·m ⁻¹]

<Subscript>

B	= bulk phase
i	= component i
M	= mixture
S	= surface

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