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Measurement of Surface Tension of Liquid Ga-Base Alloys by a Sessile Drop Method

The surface tensions and the molar volumes of liquid Ga–Bi, Ga–Sn, Ga–In, Sn–Bi, In–Bi and Sn–In binary alloys, and liquid Ga–Bi–Sn and Ga–Bi–In ternary alloys have been measured at 873 K by the sessile drop method. In addition, the calculation of the surface tension of the above binary alloys has been carried out to interpret the composition dependences of the surface tension of Ga-base liquid alloys from the thermodynamic point of view.

Keywords: Thermodynamics; Molar volume; Surface tension; Sessile drop method

1 Introduction

The authors have been studying the thermodynamics of the surface tension of liquid alloys, molten salt mixtures and molten oxide mixtures, and the interfacial tension between liquid steel and molten slag [94Tan, 96Tan, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 01Tan, 99Ued]. Since the alloys, which consist of Ga, Sn, Bi and In, are important components for compound semiconductors or Pb-free soldering materials, the information on the surface tension of those liquid alloys are indispensable for the evaluation of their crystal growth and wettability etc. However, the experimental information on them has not been accumulated enough so far to understand the effect of the thermodynamic interactions among Ga, Sn, In and Bi on the surface tension of the liquid alloys, especially in ternary systems although the surface tension of some binary alloys, e.g., Bi–Sn [56Tay], In–Sn [68Kov], In–Bi [68Kov], Ga–Bi [71Suk], Ga–In [72Kon], Ga–Sn [72Suk, 76lbr] have been reported so far below 600 K.

The purpose of this work is to measure the surface tensions and the molar volumes of liquid Ga–Bi, Ga–Sn, Ga–In, Sn–Bi, In–Bi and Sn–In binary alloys, and liquid Ga–Bi–Sn and Ga–Bi–In ternary alloys by using a sessile drop method in order to make clear the composition dependence of the physical properties of these alloys at 873 K.

2 Experimental

In the present work, we have used the sessile drop method to measure the surface tension of liquid alloys. Figure 1 shows the experimental apparatus. The furnace is heated by Ni–Cr resistance wire, and its temperature is controlled within ± 1 K by a PID controller. The temperature of the

sample is determined with a Pt–Pt(13%)Rh thermocouple located under the substrate. The present measurement of the surface tension of liquid Ga-base alloys was carried out at 873 K in order to obtain mainly the composition dependence of the surface tension of the alloys. Graphite substrate, which is polished and washed cleanly, was set on the alumina pedestal in a uniform-temperature area and accurately levelled. The reaction tube (5.5 cm outer \varnothing , 5.0 cm inner \varnothing , 20.0 cm high) is a silica tube.

The atmosphere in the furnace is hydrogen gas, which is flown in the gas-cleaning unit to remove a tiny contamination of water and oxygen. The silica tube was evacuated with a mechanical pump and backfilled with high-purity hydrogen. The specimens used in the present work were 99.999% purity metals of Ga, Sn, In, and Bi. The alloy for any desired composition is made in the crucible, which is located above the substrate. After the specimens are melted and alloyed, the specimen is dropped on the substrate from a small hole at the bottom of the crucible. The actual droplet size is 6–8 mm in the equator diameter and 4–6 mm high. The drop shadow profile was taken using a CCD camera fitted with a 70–210 mm zoom allowing magnification. The shape of the drop was determined using image analysis software. Then, this drop profile was used to determine the

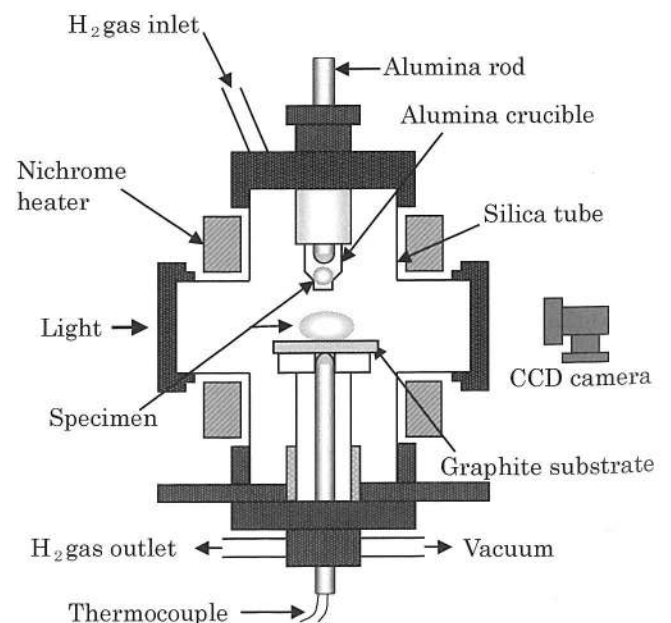


Fig. 1. Schematic diagram of the experimental apparatus.

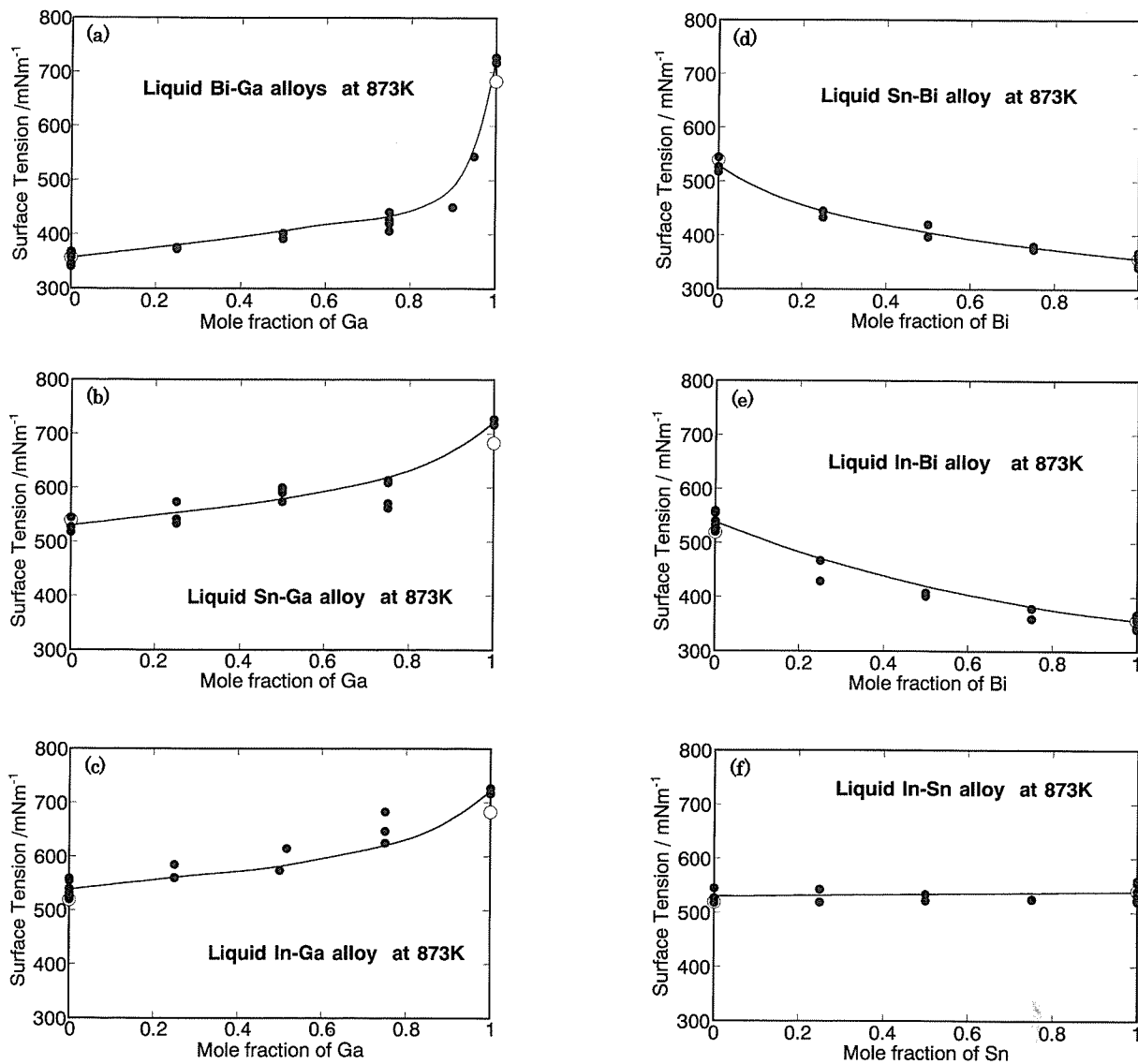


Fig. 2. Surface tension at 873 K of liquid Bi-Ga (a), Sn-Ga (b), In-Ga (c), Sn-Bi (d), In-Bi (e), and In-Sn (f) alloys. • Exp; — calc; ○ Keene [93Kee].

surface tension by comparing the observed shape with that of the solution to the Laplace equation with the surface tension as a fitting parameter, using the computational method developed by Krylov et al. [93Kry]. The molar volumes of the alloys were also obtained from the shape of the droplet.

3 Experimental Results

Figures 2a-f show the experimental results on the surface tension of liquid Ga-Sn, Ga-Bi, Ga-In, Sn-Bi, Bi-In and Sn-In alloys at 873 K. The plots indicated as open circle for the surface tension of the pure components in these figures are the suggested values from the compilation of the surface tension of pure liquid metals by Keene [93Kee], which are listed in Table 1. In addition, the curves in Figs. 2a-f are the calculated results of the surface tension of these liquid alloys, which are described in the next Section. As shown in these figures, the surface tension of liquid Ga-Bi alloys decreases drastically with increasing Bi content although the surface tension of other liquid alloys changes smoothly with the composition.

Figures 3a and b show the experimental results of the surface tension of liquid Ga-Bi-Sn and Ga-Bi-In ternary alloys, respectively. The surface tension of these ternary alloys was measured with the concentration of Ga along the composition lines of $N_{Bi} : N_X$ ($X = Sn$ or In) = 1 : 3, 1 : 1 and 3 : 1. In Figs. 3a and b, the dotted curves indicate the surface tension of the binary alloys included in the above ternary systems. As shown in these figures, the surface tensions of these ternary alloys change drastically with Ga content when the ratio of N_{Bi}/N_X ($X = Sn$ or In) increases. In other words, the effect of Bi on the surface tension is remarkable in the same way as that of the Ga-Bi alloy.

Table 1. Surface tension of liquid metals suggested by Keene [93Kee].

Metal	$\sigma_X / \text{mN} \cdot \text{m}^{-1}$	σ_X at 873 K / $\text{mN} \cdot \text{m}^{-1}$
Ga	$\sigma_{Ga} = 724 - 0.072 \cdot (T - 303)$	683
Sn	$\sigma_{Sn} = 585.7 - 0.124 \cdot (T - 505)$	540
Bi	$\sigma_{Bi} = 389 - 0.097 \cdot (T - 543)$	357
In	$\sigma_{In} = 561 - 0.095 \cdot (T - 430)$	519

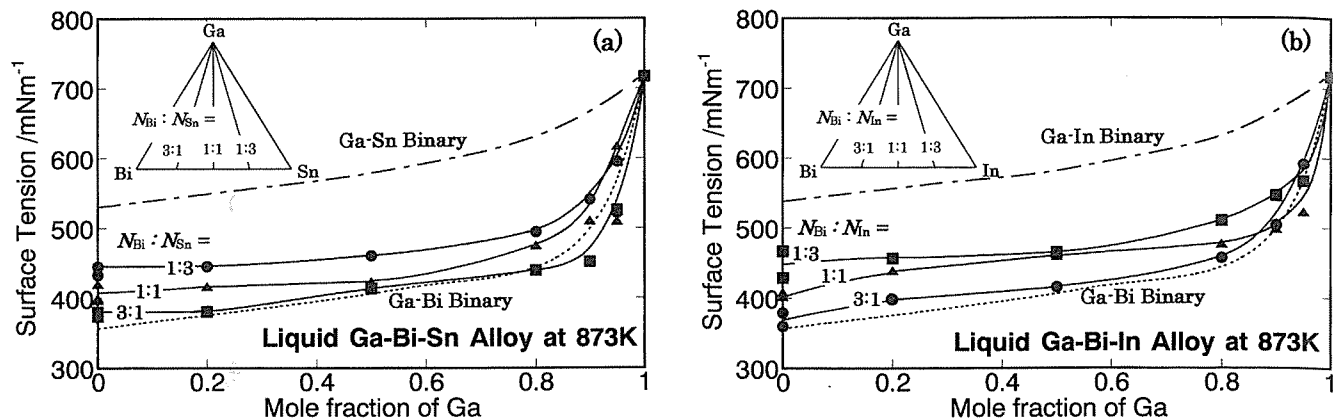


Fig. 3. Surface tension at 873 K of liquid Ga-Bi-Sn (a) and Ga-Bi-In (b) alloys. ●, ■, ▲ Exp.

Figures 4a-f show the experimental results on the molar volume of the above binary alloys. As can be seen from these figures, all of these alloys indicate the simple additivity of the composition dependence of the molar volume although the surface tensions show a downward curvature

of their composition dependence as described above. The molar volumes of liquid Ga-Bi-Sn and Ga-Bi-In alloys are shown in Figs. 5a and b. As shown in these figures, the simple addivities of the composition dependences of the molar volumes are held in these ternary alloys.

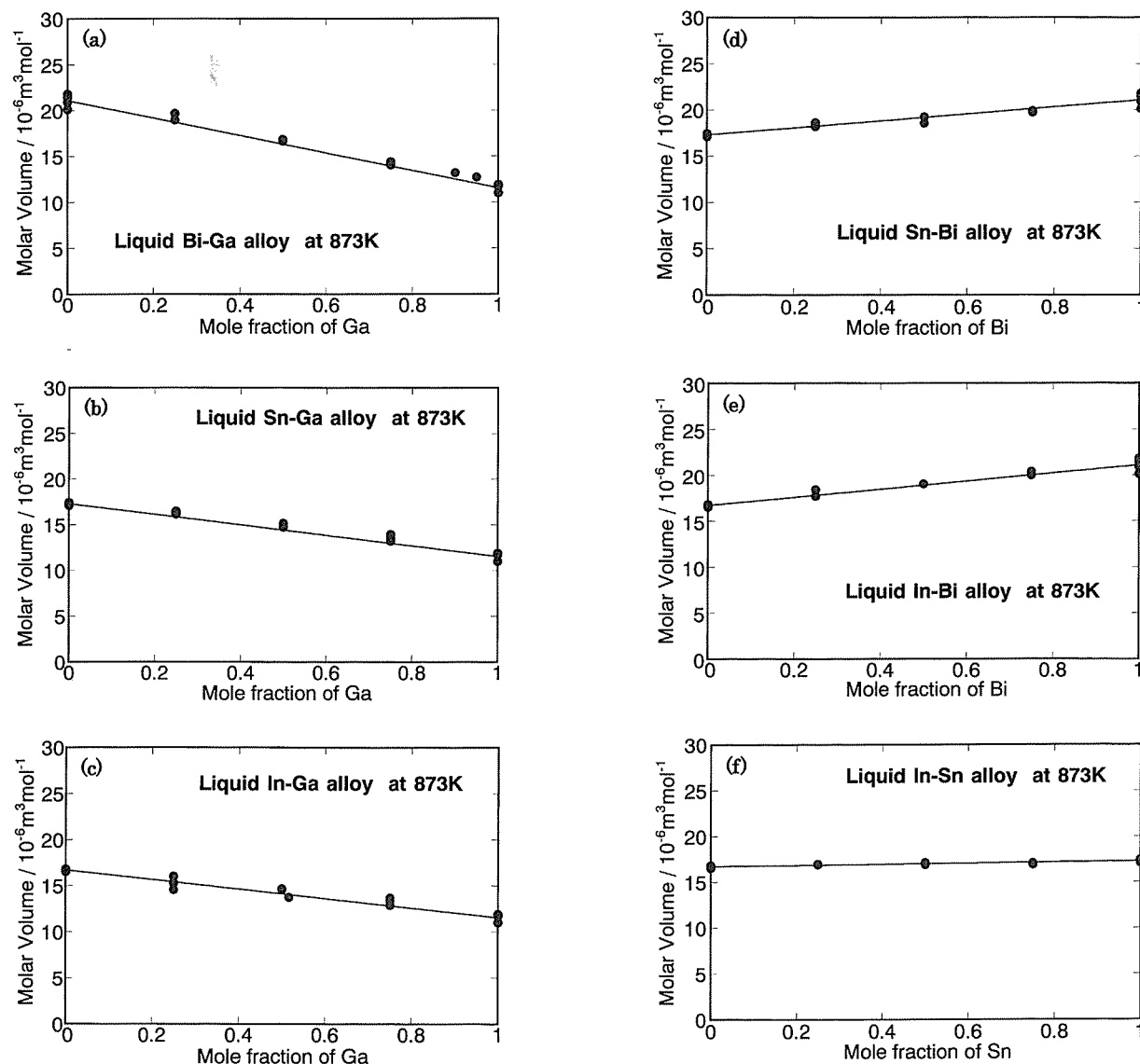


Fig. 4. Molar volume at 873 K of liquid Bi-Ga (a), Sn-Ga (b), In-Ga (c), Sn-Bi (d), In-Bi (e), and In-Sn (f) alloys. ● Exp; — additivity.

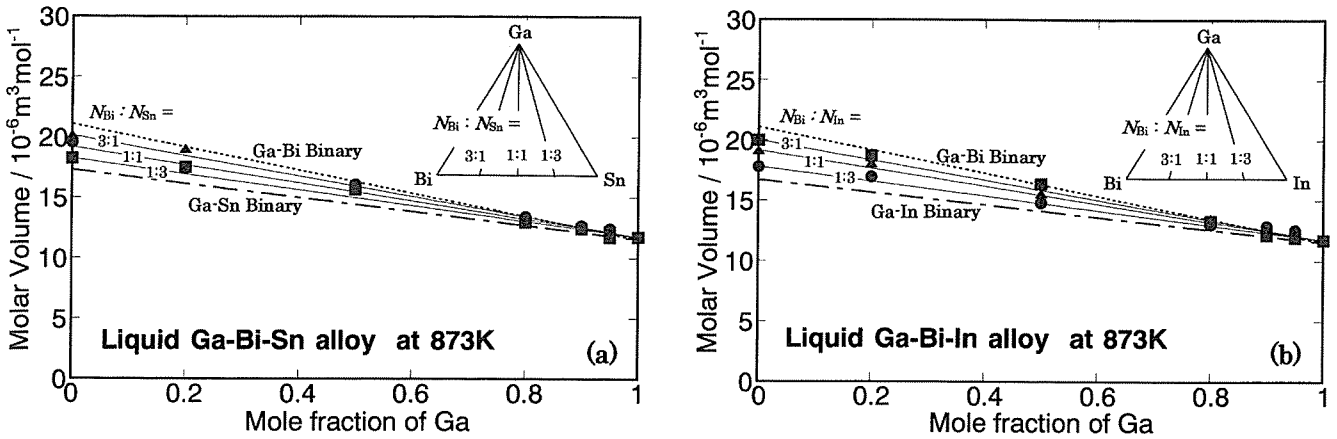


Fig. 5. Molar volume at 873 K of liquid Ga–Bi–Sn (a) and Ga–Bi–In– (b) alloys. \circ , \square , \triangle Exp; — additivity.

4 Calculation of Surface Tension of Liquid Binary Alloys

Butler's equation [32But] has been selected to calculate the surface tension of liquid alloys, thus making direct use of thermodynamic databases as described in detail in previous works [94Tan, 96Tan, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 99Ued]. Butler's equation for an A–B binary alloy is given in Eqs. (1a) and (1b):

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \left(\frac{1 - N_B^S}{1 - N_B^B} \right) + \frac{1}{A_A} \{ G_A^{E,S}(T, N_B^S) - G_A^{E,B}(T, N_B^B) \} \quad (1a)$$

$$\sigma = \sigma_B + \frac{RT}{A_B} \ln \left(\frac{N_B^S}{N_B^B} \right) + \frac{1}{A_B} \{ G_B^{E,S}(T, N_B^S) - G_B^{E,B}(T, N_B^B) \} \quad (1b)$$

In the above equations, σ_X ($X = A$ or B) is the surface tension of pure liquid metal X and A_X ($X = A$ or B) is the molar surface area of pure liquid metal X , which is obtained from the molar volume V_X of pure liquid X using Eq. (2):

$$A_X = 1.091 N_0^{1/3} V_X^{2/3} \quad (2)$$

where N_0 is the Avogadro number.

In Eqs. (1a) and (1b), the superscripts S and B indicate the surface and the bulk, respectively. $G_A^{E,P}(T, N_B^P)$ and $G_B^{E,P}(T, N_B^P)$ ($P = S$ or B) are the partial excess Gibbs energies of components A and B. These are functions of temperature T and mole fraction N_B as given in the parentheses. The partial excess Gibbs energies in the bulk $G_A^{E,B}(T, N_B^B)$ and $G_B^{E,B}(T, N_B^B)$ can be obtained directly from thermodynamic databases. For the surface, the following Eq. (3) is used:

$$G_X^{E,S}(T, N_B^S) = \beta \cdot G_X^{E,B}(T, N_B^S) \quad (3)$$

Equation (3) is based on the model proposed by Speiser et al. [87Spe, 89Yeu]. This equation means that the excess Gibbs energy in the surface has the same temperature and composition dependence as that in the bulk, but the mole fraction N_B^B is replaced by the mole fraction N_B^S in the surface. In addition, a coefficient β is multiplied to the right-

hand side. This β comes mainly from the difference between the coordination number in the bulk and that in the surface. The value of β was, however, determined to be 0.83 for liquid alloys by considering the relaxation structure of the surface of liquid metals in previous works [96Tan, 98Tan1].

The surface tension, σ , of liquid alloys can be calculated from Eqs. (1)–(3) as follows:

1. Setting temperature T and composition N_B^B of a solution.
2. Inserting the values for surface tension σ_X and molar volume V_X of pure liquid substances at the above temperature in Eqs. (1a) and (1b).
3. Determining the excess Gibbs energies in the bulk phase at the above temperature and composition, and substituting them in Eqs. (1a) and (1b).
4. Then, Eqs. (1a) and (1b) become the simultaneous equations with unknown N_B^S and σ . These equations are solved for those unknown N_B^S and σ numerically.

The data necessary for the calculation of the surface tension are listed in Table 2 [88Che, 88Iid, 92Sci, 94Ans, 94Oht]. The calculated results of the surface tension of liquid Ga–Bi, Ga–Sn, Ga–In, Sn–Bi, In–Bi and Sn–In alloys are shown in Figs. 2a–f with the experimental results. As shown in these figures, the calculated results agree well with the experimental values. In the previous works [96Tan, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 99Ued], we found that as an alloy has larger positive value of its excess Gibbs energy in the bulk, the surface tension shows more downwards curvature of its composition dependence. Therefore, the drastic decrease of the surface tension of liquid Ga–Bi alloys with the addition of Bi in Fig. 2a stems from the strong repulsive interaction between Ga and Bi since the excess Gibbs energy of liquid Ga–Bi has the largest positive value as shown in Table 2. In addition, the liquid Sn–In alloy shows the ideal behavior of the surface tension as well as the bulk thermodynamic properties because the excess Gibbs energy of this alloy is zero as indicated in Table 2.

5 Concluding Remarks

The surface tensions of liquid Ga–Bi, Ga–Sn, Ga–In, Sn–Bi, In–Bi and Sn–In binary alloys and liquid Ga–Bi–Sn

Table 2. Data used for the calculation of the surface tension of liquid binary alloys.

Molar volume $V_X/m^3 \cdot \text{mol}^{-1}$ of pure components [88Iid]	
Ga:	$V_{\text{Ga}} = 11.4 \cdot 10^{-6} \cdot \{1.0 + 0.000092 \cdot (T - 302.93)\}$
Sn:	$V_{\text{Sn}} = 17.0 \cdot 10^{-6} \cdot \{1.0 + 0.000087 \cdot (T - 504.99)\}$
Bi:	$V_{\text{Bi}} = 20.80 \cdot 10^{-6} \cdot \{1.0 + 0.000117 \cdot (T - 544.1)\}$
In:	$V_{\text{In}} = 16.3 \cdot 10^{-6} \cdot \{1.0 + 0.000097 \cdot (T - 429.55)\}$
Surface tension $\sigma_X/N \cdot \text{m}^{-1}$ of pure components at 873 K obtained by the present experiment	
Ga:	0.723
Sn:	0.530
Bi:	0.357
In:	0.538
Excess Gibbs Energy of Liquid A-B Alloys	
$G^{\text{Ex}} = N_B \cdot (1 - N_B) \cdot \{A + B \cdot (1 - 2 \cdot N_B) + C \cdot (1 - 2 \cdot N_B)^2 + D \cdot (1 - 2 \cdot N_B)^3\} / J \cdot \text{mol}^{-1}$	
Liquid Bi-Sn Alloy [94Oht]	
A = 490.0 + 0.97 · T	B = -30.0 - 0.235 · T C = 0.0 D = 0.0
Liquid Ga-Bi Alloy [92Sci]	
A = 8401.6 - 0.996135 · T	B = -560.9 + 2.43423 · T
C = 754.8 + 0.682275 · T	D = -1162.5
Liquid Ga-In Alloy [92Sci]	
A = 4450.0 + 1.19185 · T	B = 0.25943 · T C = 0.0 D = 0.0
Liquid Ga-Sn Alloy [92Sci]	
A = 3369.7 - 0.03854 · T	B = 528.9 + 0.1145 · T C = 0.0 D = 0.0
Liquid Bi-In Alloy [92Sci]	
A = -7165.05 - 0.37539 · T	B = 1503.80 - 0.54180 · T
C = 1221.15 - 1.65957 · T	D = -1627.00 + 2.76395 · T
Liquid Sn-In Alloy	
A = 0.0	B = 0.0 C = 0.0 D = 0.0

and Ga-Bi-In alloys have been measured at 873 K by the sessile drop method. In addition, the surface tensions of liquid binary alloys were calculated from the thermodynamic properties to make clear the composition dependence of the surface tension of these alloys. Especially, it is found that the surface tensions of liquid Ga-base alloys are affected by the strong repulsive interaction between Ga and Bi. On the other hand, the composition dependences of the molar volumes show the simple additivity in the above binary and ternary systems of Ga-base liquid alloys.

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