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Surface Tension of the Liquid Hg-In Alloys

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The measurements of the surface tension of the liquid Hg-In alloys were made by means of a maximum drop pressure method. The surface tension increases monotonously with increasing the In concentration. It is thermodynamically shown that the composition of the Hg atoms adsorbed on the surface is larger than that in the bulk. Experimental results are compared with calculated results due to various model theories; in particular the hard sphere model with a density-dependent cohesive potential is found to be in qualitative agreement with experimental results of both surface tensions and its temperature coefficients.

1 INTRODUCTION

This paper describes results of the surface tension measurements of liquid Hg-In alloys. Previous measurements of surface tension of this system (except for the respective pure states) have been reported by Olsen and Johnson,¹ but their study has been limited to the Hg-rich region at 25°C. The Hg-In system, in which both components have negative activity coefficients^{2,3} and nearly equal atomic volumes, has been investigated mainly from the point of view of bulk properties, such as electron transport^{4,5} and viscosity.⁶ It is also important to investigate surface properties, such as the surface tension of the Hg-In system over the entire composition range. The experimental data are discussed using three kinds of theoretical models; the concentration fluctuation theory, lattice theory and density-dependent pseudo-potential theory.

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2 EXPERIMENTAL

2.1 Method and procedure

The surface tension was measured using a maximum drop pressure technique.⁷ A simple glass cell, which consisted of a capillary part and a metal reservoir as illustrated in Figure 1, was filled with the alloys in vacuo and then sealed off from the vacuum system. The cell was attached to the driving apparatus for its rotation in an oil bath. The change in the level difference (with the rate of about 0.2 mm/min) was read by a cathetometer, and the maximum height was determined at the instant when the metal began to flow upwards vertically out of the capillary. The pressure needed to make the alloy overflow was gradually applied to the samples by turning the cell.

The surface tension γ was, thus, calculated by Schrödinger's equation⁸

$$\gamma = \frac{1}{2} r g \rho_m h \left[1 - \frac{2}{3} \left(\frac{r}{h} \right) - \frac{1}{6} \left(\frac{r}{h} \right)^2 \right], \quad (1)$$

in which h is the height of liquid, r the radius of capillary, ρ_m the density and g the acceleration of gravity.

The alloys were prepared from Hg (99.998%), distilled twice, and In (99.9999%) in vacuo. The inner diameter of capillary (0.3 ~ 0.4 mm) was measured using a microscope after each measurement. Density data used were taken from those reported by Predel and Eram.⁹ Experimental errors are within $\pm 1\%$.

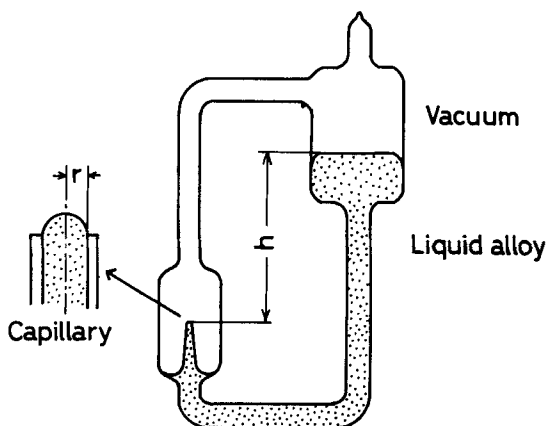


FIGURE 1 Cell used for the maximum drop pressure method.

2.2 Results

The surface tension data are plotted against temperature and composition in Figures 2 and 3, respectively. Our value $482 \pm 5 \text{ mNm}^{-1}$ for pure Hg at 20°C is in good agreement with that in literature¹⁰ $485 \pm 1.2 \text{ mNm}^{-1}$ at 25°C . The value of 566 mNm^{-1} for pure In at 160°C is slightly higher than that of Hoar and Melford,¹¹ $559 \pm 5 \text{ mNm}^{-1}$.

The surface tension increases monotonously with increase of the In concentration at all the temperatures. The values of Olsen and Johnson,¹ whose composition range was below 64 at. % In, are also in good agreement with our data except for that of 64 at. % In.

No anomalous behaviour of the composition dependence is observed in the isotherm of surface tension within experimental errors. The slightly convex nature of the curve i.e., the positive deviations from the linear law, being indicated by a dotted line in Figure 3, should be noted.

3 DISCUSSION

3.1 Surface segregation estimated by Gibbs' adsorption equation

The surface tension of binary mixtures is related to the surface adsorption by Gibbs' adsorption equations,¹²

$$\frac{\partial\gamma}{\partial x_\alpha} = - \left(\frac{\Gamma_\beta - x_\beta \Gamma_\alpha}{x_\alpha} \right) \frac{\partial\mu_\beta}{\partial x_\beta}, \quad (2)$$

where, Γ_α denotes the number of moles of the component α in unit area of the surface layer, x_α , the atomic fraction and μ_α the chemical potential of the component α . The quantities $\Gamma_\beta - x_\beta \Gamma_\alpha/x_\alpha$ can be calculated from Eq. (2) using the activity results of this system² and the present surface tension data.

By assuming that the surface is monolayer and that the surface area of each component per mole A_α is of the same as that in the pure state A_α^0 , an additional relation between Γ_α and Γ_β is obtained.¹²

$$A_\alpha^0 \Gamma_\alpha + A_\beta^0 \Gamma_\beta = 1. \quad (3)$$

The value of A_α^0 was estimated from the density data by the relation $A_\alpha^0 = (V_\alpha^0)^{1/3} N^{1/3}$, where V_α^0 and N represent the molar volume of component α in the pure state and Avogadro's number respectively; the estimated values of A_α^0 were $4.37 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$ for Hg and $4.58 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$ for In at 433 K. As can be seen in Table 1, the calculated surface atomic fraction of Hg (i.e., $\Gamma_{\text{Hg}}/(\Gamma_{\text{Hg}} + \Gamma_{\text{In}})$) is larger than the bulk atomic fraction, x_{Hg} .

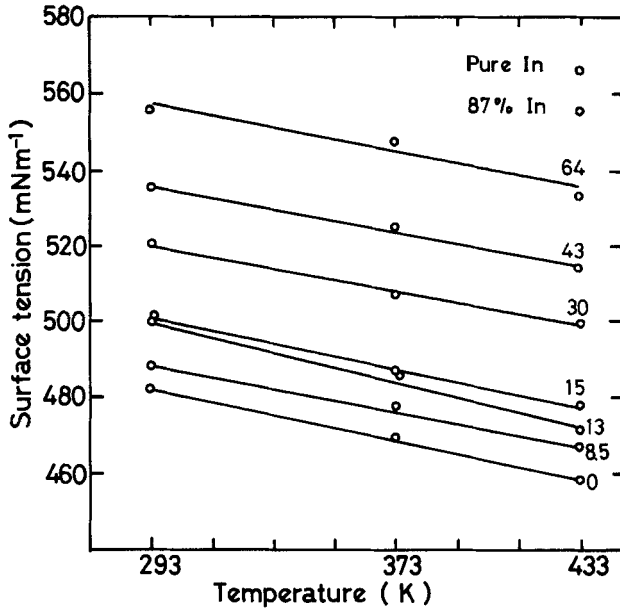


FIGURE 2 Temperature dependence of the surface tension of liquid Hg-In system.

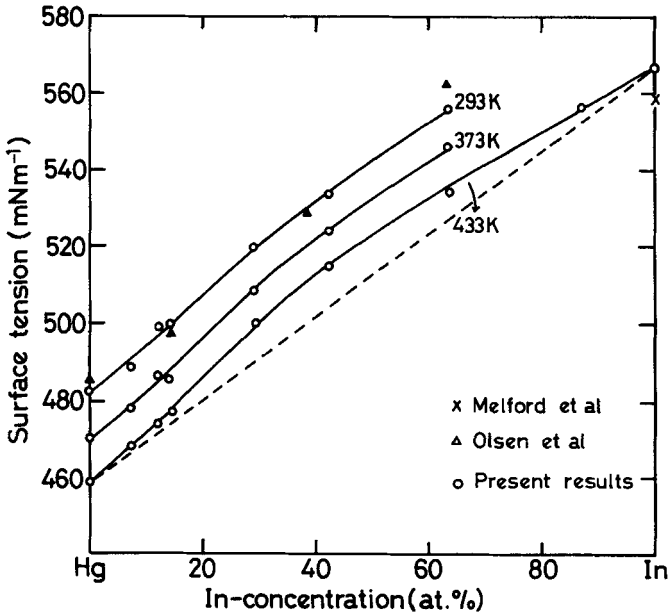


FIGURE 3 Concentration dependence of the surface tension of liquid Hg-In system.

TABLE I
Surface adsorption and composition of the Hg-In system at 433 K

x_{Hg}	$\Gamma_g - X_{\text{Hg}}\Gamma_{\text{In}}/X_{\text{In}}$	Γ_{Hg}	Γ_{In}	$\Gamma_{\text{Hg}}/(\Gamma_{\text{Hg}} + \Gamma_{\text{In}})$
(bulk)		10^{-6} moles m^{-2}		(surface)
0.0	0.0	0.0	21.8	0.0
0.2	1.9	5.9	16.2	0.27
0.4	3.9	11.3	11.1	0.50
0.6	8.1	16.8	5.8	0.74
0.8	21.2	22.5	0.3	0.99
1.0	—	22.9	0.0	1.0

3.2 The analysis due to concentration fluctuation theory

Bhatia and March¹³ developed the theory of surface tension of liquid alloys by extending Cahn–Hilliard’s concentration fluctuation theory¹⁴ for surface tensions. Their expression for the surface tension of alloys, γ_M , is of the form

$$\gamma_M \sim \frac{l}{\chi_T} \left(1 + \frac{\delta^2 S_{cc}(0)}{nk_B T \chi_T} \right)^{-1} \quad (4)$$

Here n , k_B , T and χ_T represent the number density, the Boltzmann’s constant, absolute temperature and the isothermal compressibility respectively. The $S_{cc}(0)$ is the long wavelength limit of the liquid structure factor which can be written as

$$S_{cc}(0) = nk_B TV(\partial^2 G/\partial x_\alpha^2)^{-1}, \quad (5)$$

where G is the Gibbs free energy and V the volume. The δ is the size factor defined by

$$\delta = \frac{1}{V} \left(\frac{\partial V}{\partial x_\alpha} \right)_{T,P,N} = \frac{v_\alpha - v_\beta}{x_\alpha v_\alpha + x_\beta v_\beta} \quad (6)$$

with the partial molar volume v_α of the component α . The surface tensions for the liquid Hg–In alloys can thus be estimated by Eq. (4) as far as values of χ_T , δ , $S_{cc}(0)$ and the surface thickness l are known. For this estimation the linear relation was assumed for χ_T and l ; experimental χ_T values of pure Hg and In were used and the surface thickness of pure metals were determined by fitting the calculated surface tension values to experimental ones (0.223 Å for Hg and 0.168 Å for In, which are almost the same as those determined by Bhatia and March¹³ for polyvalent liquid metals). The size factor δ was calculated by assuming that v_i in the alloys is equal to v_i^0 in the pure state. This simplification may be reasonable for this system because its excess volume of mixing is very small. Values of $S_{cc}(0)$ were calculated by activity data of Okajima and Shimoji.² For comparison, similar calculations were

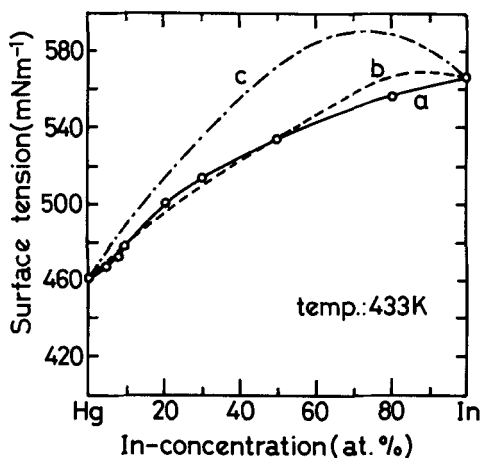


FIGURE 4 Comparisons of the surface tensions calculated from the concentration fluctuation theory and experiment. a: experiment; b: $S_{cc}^{real}(0)$; c: $S_{cc}^{ideal}(0)$.

also made by assuming ideal mixing; that is $S_{cc}(0) = S_{cc}^{id}(0) = x_{\alpha}x_{\beta}$. Figure 4 shows that calculated results in which real $S_{cc}(0)$ was used are in better agreement with experiment than those due to $S_{cc}^{id}(0)$.

3.3 The lattice model calculation

Many lattice theories for surface tension of liquid mixtures have been presented on the basis of the monolayer^{15,16} or multi-layer models.¹⁷ These theories can be conveniently applied to liquid alloys in spite of the hypothetical structure pictures. Here, Guggenheim's theory¹⁵ and Hoar-Melford's theory¹⁶ were used which can be written

$$\begin{aligned} \gamma_M &= \gamma_{\alpha} + \frac{RT}{A_{\alpha}} \ln \frac{x'_{\alpha}}{x_{\alpha}} + \frac{pW}{A_{\alpha}} x'_{\beta} - \frac{(p+q)}{A_{\alpha}} Wx_{\beta}^2 \\ &= \gamma_{\beta} + \frac{RT}{A_{\beta}} \ln \frac{x'_{\beta}}{x_{\beta}} + \frac{pW}{A_{\beta}} x'_{\alpha} - \frac{(p+q)}{A_{\beta}} Wx_{\alpha}^2. \end{aligned} \quad (7)$$

These two theories are based on the regular solution theory and are characterized by the regular solution parameter W ($W = \Delta H^M/x_{\alpha}x_{\beta}$; ΔH^M being the enthalpy of mixing). In Eq. (7), γ_{α} represents the surface tension value of component α in the pure state; R is the Gas constant; x_{α} represents bulk atomic fraction of α and prime indicates the surface atomic fraction; A_{α} is the surface area per mole of α component in the alloys. Guggenheim's model corresponds to the case where $A_{\alpha} = A_{\beta} = A$.

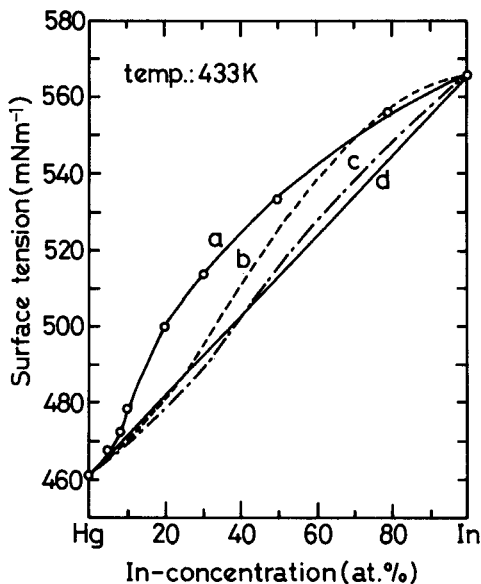


FIGURE 5 Comparisons of the surface tensions calculated from the lattice model theory and experiment. a: experiment; b: Hoar-Melford theory; c: Guggenheim theory; d: linear law.

The parameters p and q have the meaning of the fraction of the total next-neighbour contacts made by a molecule within its own layer and that in either adjoining layer. For numerical calculations, $p = 1/2$ and $q = 1/4$ were assumed, which corresponds to a close packing structure. In the treatment of Hoar and Melford the values of p and q can be slightly varied by some relaxation effect of the surface layer, though the condition $p + q = 1$ is required; here, the value of p was assumed to be 0.75 as in their paper.

Figure 5 shows that calculated results are in good agreement with experiment in the In-rich concentration range, in particular in the case of Hoar-Melford's theory, but in the Hg-rich region slight negative deviations from the linear law are predicted, in contradiction to experiments. In these calculations the surface enrichment of Hg atom was confirmed, which is similar to the thermodynamic analysis given in Table 1.

3.4 The analysis due to the hard sphere model in a density-dependent cohesive potential

We can derive the expression for the surface tension of hard sphere fluids enclosed in a density-dependent cohesive potential from the point of view of the more general neutral pseudo-atom theory of the surface tension of liquid metals presented by Evans.¹⁸ His formalism, based on the pseudo-potential

theory, stresses the importance of the density-dependent but structure-independent energy $u_g(n)$ (n : electron density) at the surface. Extension of this theory to the liquid alloy state is straightforward. The total potential energy Φ of liquid alloys can be described by the sum of $u_g(n)$ part and the part containing pair-potential $\phi_{\alpha\beta}(R_{ij}; n)$ between the i -th atom of the species α and the j -th atom of the species β . Assuming that the density gradient is only possible to the direction z normal to the surface, we have for the surface tension of liquid alloys

$$\begin{aligned} \gamma_M = & - \int_{-\infty}^{\infty} dz z \frac{\partial u_g(n(z))}{\partial z} (\rho_\alpha(z) + \rho_\beta(z)) \\ & - \frac{1}{2} \int_{-\infty}^{\infty} dz_1 z_1 \int dR_{12} \left[\frac{\partial \phi_{\alpha\alpha}}{\partial z_1} n_{\alpha\alpha}^{(2)}(R_{12}) + \frac{\partial \phi_{\beta\beta}}{\partial z_1} n_{\beta\beta}^{(2)}(R_{12}) \right. \\ & \left. + 2 \frac{\partial \phi_{\alpha\beta}}{\partial z} n_{\alpha\beta}^{(2)}(R_{12}) \right] + \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int dR_{12} \frac{(x_{12}^2 - z_{12}^2)}{R_{12}} \\ & \times \left[\frac{\partial \phi_{\alpha\alpha}}{\partial R_{12}} n_{\alpha\alpha}^{(2)}(R_{12}) + \frac{\partial \phi_{\beta\beta}}{\partial R_{12}} n_{\beta\beta}^{(2)}(R_{12}) + 2 \frac{\partial \phi_{\alpha\beta}}{\partial R_{12}} n_{\alpha\beta}^{(2)}(R_{12}) \right]. \end{aligned}$$

In this expression, $\rho_\alpha(z)$ is the ion number density of the species α and $n_{\alpha\beta}^{(2)}(R_{ij})$ represents the two particle density correlation function between the particle of species α and that of species β at the separation of R_{ij} .

The second term in Eq. (8) caused by the density dependence of interionic potentials can be neglected in comparison with the first term arising from the density dependent potential u_g . For numerical calculations, it was assumed that at the surface the exponential decay of electron density and the step functional profile of ion density were assumed;¹⁸ the radial distribution function at the surface can thus be replaced by that of bulk. The last integral term in Eq. (8) thus leads to a simple extension of Fowler's expression¹⁹ for the surface tension of mixtures, in which the surface segregation effect is neglected. Because reliable interionic potentials in liquid alloys are still unavailable generally, hard sphere potentials are simply assumed for interionic potentials; this approximation was successful in bulk liquid metals.²⁰ These simplifications in Eq. (8) give

$$\begin{aligned} \gamma_M = & - \frac{1}{2} (\rho_\alpha^0 + \rho_\beta^0) L n^0 \left[\frac{\partial u_g(n^0)}{\partial n^0} \right] \\ & - \frac{\pi}{8} k_B T [\rho_\alpha^{02} \sigma_{\alpha\alpha}^4 g_{\alpha\alpha}^H(\sigma_{\alpha\alpha}) + \rho_\beta^{02} \sigma_{\beta\beta}^4 g_{\beta\beta}^H(\sigma_{\beta\beta}) \\ & + 2\rho_\alpha^0 \rho_\beta^0 \sigma_{\alpha\beta}^4 g_{\alpha\beta}^H(\sigma_{\alpha\beta})], \end{aligned} \quad (9)$$

where L represents the electron decay distance at the surface and the superscript 0 indicates the bulk quantity; $\sigma_{\alpha\alpha}$, $\sigma_{\alpha\beta}$ and $\sigma_{\beta\beta}$ are the closest distance of approach between $\alpha - \alpha$, $\alpha - \beta$ and $\beta - \beta$ atoms. Radial distribution functions at the hard sphere diameter $g_{\alpha\alpha}^H(\sigma_{\alpha\alpha})$, $g_{\alpha\beta}^H(\sigma_{\alpha\beta})$ and $g_{\beta\beta}^H(\sigma_{\beta\beta})$ can be given as the solution of the PY equation of mixture of hard spheres.²¹

The structure-independent term u_g can be calculated by extending Heine and Weair's expression²² to alloy states

$$u_g(R_a) = \frac{2.21Z^{*5/3}}{R_a^2} - \frac{0.916Z^{*4/3}}{R_a} + Z^*E_{CR} - \frac{1.8Z^{*2}}{R_a} + \frac{3Z^*(ZR_M^2)^*}{R_a^3} - \frac{Z^*}{R_a^3}(A_0R_M^3)^* \text{ rydberg.} \quad (10)$$

where R_a is the radius of the atomic sphere, E_{CR} is the correlation energy of electron gas and given in the form $E_{CR} = 0.0313 \ln(R_a/Z^{*1/3}) - 0.100$ ryd. The pseudopotential parameter R_M and A_0 represent the core size and the potential depth in the core region. The asterisk means the concentration average. In Eq. (10) it was assumed that two kinds of ion cores in alloys can be replaced by a single average ion core. Similar assumptions were adopted by Faber²³ in the calculation of compressibility of liquid alloys. Parameters (in atomic unit) used in Eq. (10) are as follows: $A_0 = 1.05$ and $R_M = 2.6$ for Hg, $A_0 = 1.35$ and $R_M = 2.4$ for In²⁰.

In order to determine the packing fraction y , which is related to the hard sphere diameters σ_α and σ_β by $y = \pi(\rho_\alpha^0\sigma_\alpha^3 + \rho_\beta^0\sigma_\beta^3)/6$, expressions for thermal pressure coefficient γ_v^0 and its temperature coefficient $(\partial\gamma_v/\partial T)_v$ are used.

$$\gamma_v = nk_B \left[\frac{(1 + y + y^2 - y^3)}{(1 - y)^3} + \frac{2(2 + 2y - y^2)T(\partial y/\partial T)_v}{(1 - y)^4} \right]. \quad (11)$$

$$(\partial\gamma_v/\partial T)_v = 4nk_B(2 + 2y - y^2)(\partial y/\partial T)_v(1 - y)^4 + 4nk_B T(5 + 2y - y^2)(\partial y/\partial T)_v^2/(1 - y)^5. \quad (12)$$

The experimental value of $(\partial\gamma_v/\partial T)_v$ was approximated by $(\partial\gamma_v/\partial T)_p$, which can be estimated from the temperature dependence of χ_T and thermal expansion coefficient α_p . The results are as follows: $y = 0.443$ and $(\partial y/\partial T)_v = -9.6 \times 10^{-5} \text{ K}^{-1}$ for Hg at 160°C and $y = 0.446$ and $(\partial y/\partial T)_v = -5.3 \times 10^{-5} \text{ K}^{-1}$ for In at 160°C. The electron decay distance L at the surface for pure Hg and pure In was determined in order to fit the surface tension value by Eq. (9) to the experimental value. Determined L are 0.34 Å for Hg and 0.81 Å for In respectively. These L values are reasonable in comparison with the value estimated by Evans¹⁸ from the Lang-Kohn's density functional theory²⁴ and those of Bhatia and March¹³ derived from

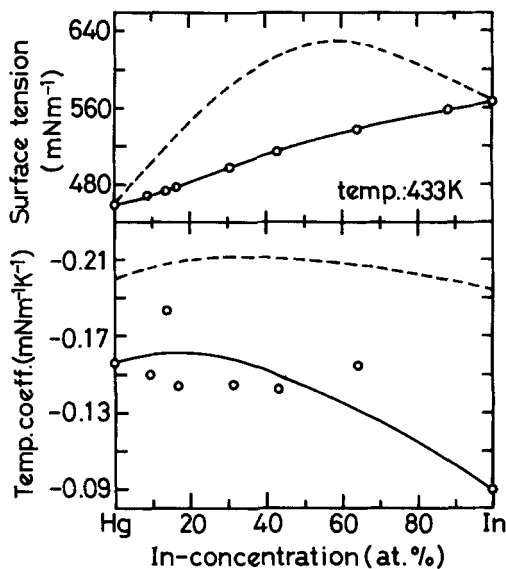


FIGURE 6 Comparisons of the surface tensions and its temperature coefficients calculated from the hard sphere model in a density dependent cohesive potential. —: experiment; - - - -: theory.

the concentration fluctuation theory. For alloys, L was estimated from the linear relation between those of pure components. Calculated results shown in Figure 6 predict the positive departure of the isotherm curve from the linear law and are qualitatively in good agreement with experiment.

In addition to the surface tension values, its temperature coefficient can be predicted by assuming that u_g term in Eq. (9) is essentially insensitive to temperature, as performed successfully for pure liquid metals.²⁵ The resulting expressions becomes

$$\frac{\partial \gamma_M}{\partial T} \cong -\frac{\pi}{8} k_B [\rho_\alpha^{02} \sigma_{\alpha\alpha}^4 g_{\alpha\alpha}^H(\sigma_{\alpha\alpha}) + \rho_\beta^{02} \sigma_{\beta\beta}^4 g_{\beta\beta}^H(\sigma_{\beta\beta}) + 2\rho_\alpha \rho_\beta \sigma_{\alpha\beta}^4 g_{\alpha\beta}^H(\sigma_{\alpha\beta})]. \quad (13)$$

Figure 6 shows that the calculated temperature coefficients are in fairly good agreement with experiment in particular in the Hg-rich concentration region.

3.5 General discussions and conclusions

The surface behavior of Hg-In alloys were predicted mostly by the concentration fluctuation theory and the model of hard sphere fluids enclosed in a density-dependent cohesive potential. In particular, the latter model was

able to predict the temperature coefficient in addition to the surface tension value. This model, which is based on the neutral pseudo-atom theory of Evans, contains the parameter of electron decay distance L at the surface. For numerical calculations, L was determined in order to fit the calculated surface tension values to experimental ones. But in principle the electron density profile must be closely linked to the ion density profile at the surface. In this respect, the self-consistent treatment of electron and ion profile by Allen and Rice²⁶ becomes important in a purely theoretical point of view. In addition to this point, there remains important problems peculiar to alloy problems, that is the surface segregation effect and the charge transfer effect. In this paper, the former is completely neglected and the latter is taken into account approximately by assuming the average values of ion cores or depth-parameters. Further improved treatments are desired to make clear such problems in the surface properties of liquid alloys.

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