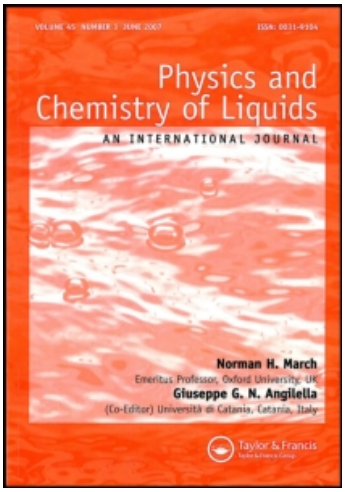

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Entropy of Mixing of Compound Forming Liquid Binary Alloys Using Flory's Formula

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We demonstrate how the formula we proposed recently for the effective volume can be applied to improve Flory's formula so that the entropy of mixing of liquid binary alloys can be determined theoretically with good accuracy. The results are distinctly better than in the hard sphere system for compound forming alloys.

1 INTRODUCTION

Flory's formula[1] for the entropy of mixing was primarily proposed for treating thermodynamic properties of high polymer solution. Later it has been extensively used for simple binary alloys having small size effects by Bhatia,[2] Tamaki and Cusack,[3] Visser *et al.*[4] and Hoshino[5]. The model incorporates few simplifications and is not particularly developed for metallic system, thus one expects qualitative agreement between experimental and theoretical values. However, the validity of the formula for treating thermodynamical properties of compound forming binary alloys has not been examined. The present work examines the applicability of Flory's formula to a wider class of binary alloys and demonstrates how the approach can be applied successfully to calculate the entropy of mixing of compound forming alloys. This improvement advances our understanding of the structural composition of these alloys.

2 FORMULATION

According to Flory[1], the entropy of mixing is given by

$$\frac{\Delta S_F}{NK_B} = -\sum_{i=1}^{c} C_i \ln \phi_i \tag{1}$$

where ϕ_i is the volume fraction and for our model can be written as

$$\phi_i = C_i \Omega_i / \Omega \tag{2}$$

where Ω is the effective volume and is expressed, following Khanna and Singh[6] and Khanna,[7] as

$$\Omega = \Omega_{\text{ideal}} + C_1 C_2 \Delta\Omega_0 \tag{3}$$

with

$$\Omega_{\text{ideal}} = C_1\Omega_1 + C_2\Omega_2.$$

$\Delta\Omega_0$ is a disposable parameter and is obtained by fitting the entropy of mixing to its experimental value at equiatomic concentration.

Now (1) is written as

$$\frac{\Delta S_F}{NK_B} = \ln\left(\frac{\Omega_F}{\Omega_1^{C_1}\Omega_2^{C_2}}\right) - S_C \tag{4}$$

with

$$S_C = C_1 \ln C_1 + C_2 \ln C_2$$

where Ω_F is the effective volume in Flory's formula defined by Eq. (3). This is equivalent to including a correction term $\ln(\Omega_F/\Omega_{\text{ideal}})$ in Flory's formula such that

$$\frac{\Delta S_F}{NK_B} = \ln \frac{\Omega_{\text{ideal}}}{\Omega_1^{C_2}\Omega_2^{C_2}} + \ln\left(\frac{\Omega_F}{\Omega_{\text{ideal}}}\right) - C_1 \ln C_1 - C_2 \ln C_2. \tag{4a}$$

The hard sphere reference system has been extensively discussed in the literature. Following Yokoyama *et al.*[8] and Hoshino,[5] the entropy of mixing can be written as

$$\Delta S_{HS} = \Delta S_{\text{gas}} + \Delta S_\eta + S_c + S_\sigma \tag{5}$$

The expressions of Eq. (5) are well known and written elsewhere.[5] Thus two expressions of the entropy of mixing in the present approach differ by

$$\Delta H_{HS} - \Delta S_{\text{Flory}} = \ln\left(\frac{\Omega_H}{\Omega_F}\right) + \Delta S_\eta + S_\sigma \tag{6}$$

here Ω_H is the effective volume of an alloy in Hard sphere system defined by Eq. (3).

3 NUMERICAL RESULTS AND DISCUSSION

In the calculation, we use Flory's formula of the entropy of mixing (Eq. 4) with the modified effective volume (Ω_F) estimated by our model. The Eq. (3) estimates the effective volume of alloys such that the entropy of mixing fits with its experimental value at equiatomic concentration. That leads to an evaluation of $\Delta\Omega_0$ which is a constant for a given alloy system and quantitatively calculates the volume of mixing at different concentrations. Then we proceed to calculate the entropy of mixing (a) for regular alloys i.e. alloys whose constituent elements have small size effects, (b) for the alloys that show the compound forming nature. Figures 1(a–c) show the excess entropy of CdIn, BiPb and BiSn binary alloys. The plot of excess entropy instead of entropy of mixing for simple alloys is due to their smaller values

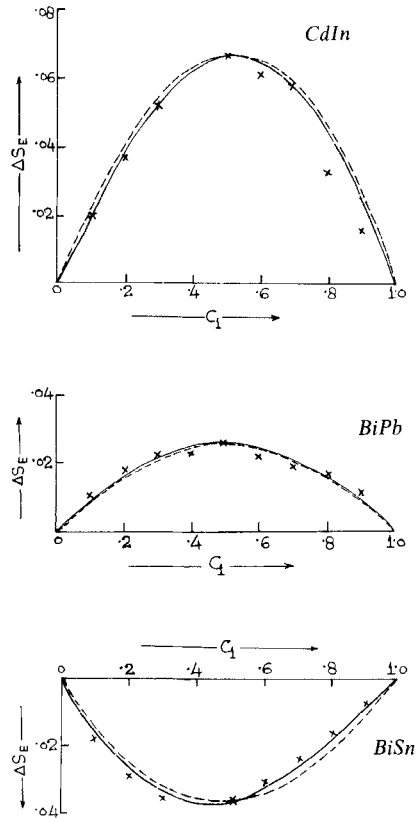

FIGURE 1(a–c) Concentration dependence of the excess entropy of regular binary alloys. Full line—Hard sphere system, dotted lines—Flory's formula and crosses represent experimental values from Hultgren *et al.*[9].

of excess entropy in comparison to ideal entropy. Finally, in the same spirit, we apply Flory's formula to determine the entropy of mixing of compound forming liquids. Liquid binary alloys of interest, NaHg, NaGa and KPb have been extensively studied by Hultgren *et al.*,[9] Singh and Khanna,[10] Tamaki and Cusack,[3] Tamaki *et al.*[11] that establish their compound forming natures. The numerical results for entropy of mixing and excess entropy at different concentrations are shown in Figures 2(a–c).

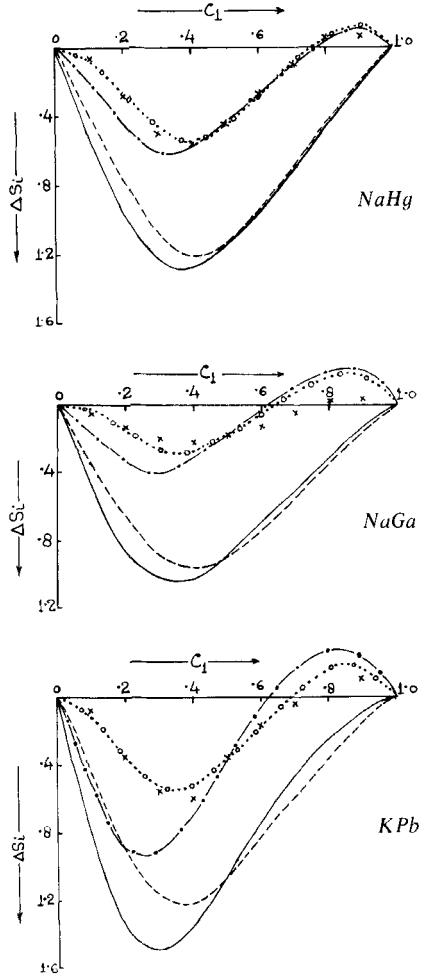

FIGURE 2(a–c) Concentration dependence of the entropy of mixing of compound forming alloys. Dash and dot—Hard sphere system, dot and circle—Flory's formula. Other curves represent the same as described in Figure 1. Experimental values are from Hultgren *et al.*[9] for NaHg and KPb alloys and from Tamaki and Cusack[3] for NaGa binary alloy.

The calculated values for simple and compound forming alloys are compared carefully with the corresponding experimental results and those obtained from hard sphere reference system.[7,10] It is noteworthy that the same formula for the effective volume has been used in the hard sphere reference system. For simple alloys, the results can be described as satisfactory to explain the entropy of mixing and compare well with those obtained by means of a hard sphere reference system. Further the task that appeared to be rather difficult for the compound forming alloys becomes easier by applying our model and the results are found quantitatively to be more consistent with the experimental data by using Flory's formula than those obtained by means of the hard sphere reference system. However, there is one aspect that is a difficulty with Flory's formula. It is that the volume of mixing leads to disaster for any reasonable choice of effective volume which has much larger magnitude of volume of mixing in Flory's formula in comparison to the hard sphere reference system as shown in Figure 3(a and b). This difference is due to the fact that Flory's formula does not involve any expression pertaining to the ΔS_η and S_σ terms considered in the hard sphere system, which leads in turn to some change in the volume of any alloy. We find that once the fitting is obtained at equiatomic concentration, both the systems yield the same results for most of the concentration compositions and Eq. (6) leads to the small values. However, in the

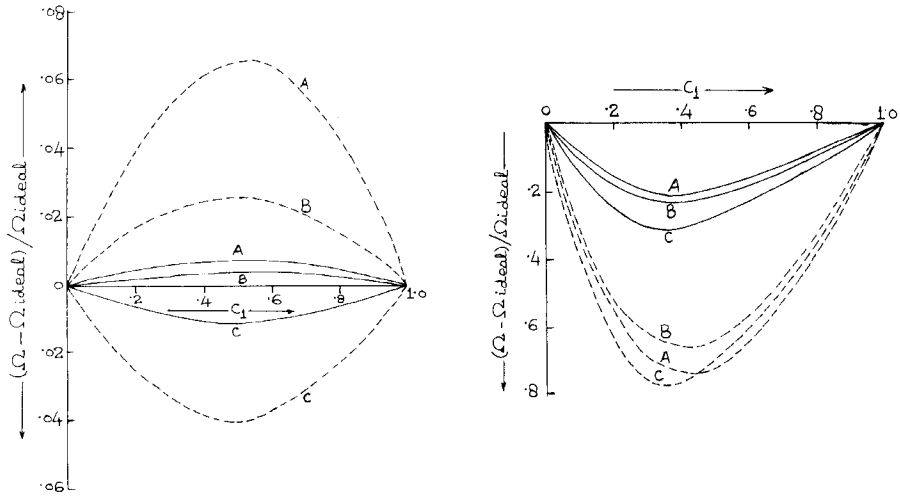

FIGURE 3(a and b) Concentration dependence of the fractional change in volume for (a) regular alloys: A. CdIn, B. BiPb, C. BiSn. (b) Compound forming alloys: A. NaHg, B. NaGa, C. KPb. Full and dotted lines represent results calculated by using Hard sphere system and Flory's formula respectively.

absence of the experimental values we cannot predict the accuracy of the volume of mixing.

4 CONCLUSION

These thermodynamic results do not give any definite answer concerning the kind of compound formed in these alloys, but it is shown that the entropy of mixing, derived in this way, contains only an additional volume of mixing term as a first approximation. This point is complementarily appreciated as nothing has been assumed concerning molecular formation. Thus, the existence of molecules as believed to date,[2,5] becomes questionable at least for metallic systems. The present method is rather general and may be applied to a large number of binary mixtures.

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