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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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**To cite this Article** March, N. H. and Alonso, J. A. (2008) 'Non-monotonic behaviour with concentration of the surface tension of certain binary liquid alloys', *Physics and Chemistry of Liquids*, 46: 5, 522 — 526

**To link to this Article:** DOI: 10.1080/00319100801930466

**URL:** <http://dx.doi.org/10.1080/00319100801930466>

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## Non-monotonic behaviour with concentration of the surface tension of certain binary liquid alloys

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(Received 14 January 2008; final version received 19 January 2008)

The surface tension  $\sigma(c)$  of most liquid binary alloys usually varies with concentration  $c$  in a monotonic way between the values  $\sigma_1$  and  $\sigma_2$  of the two pure metals, and this behaviour is well explained by current models. Some alloys show deviations from this ideal behaviour. One of those is Fe–B. The surface tension of this liquid alloy shows a minimum at 17 atomic % B, which corresponds well with the composition of the eutectic point in the phase diagram, followed by a maximum at a concentration of 24 atomic % B or higher. The usual models for the surface tension of liquid binary alloys do not explain those exceptional features, and we propose that a model involving the concentration fluctuations in the liquid alloy has the proper ingredients to account for the features in Fe–B and similar alloys.

**Keywords:** surface tension; alloys; liquid metals

The surface tension  $\sigma(c)$  of most liquid binary alloys usually varies with concentration  $c$  in a smooth way between the values  $\sigma_1$  and  $\sigma_2$  of the two pure metals [1–3]. Current theoretical models account for this behaviour. This is true for early studies, such as the thermodynamical treatment of Guggenheim [4]. This theory yields a relation between  $\sigma(c)$  and the component surface tensions  $\sigma_1$  and  $\sigma_2$  of the form

$$\exp(-\beta a^2 \sigma) = (1 - c) \exp(-\beta a^2 \sigma_1) + c \exp(-\beta a^2 \sigma_2), \quad (1)$$

where  $\beta = (k_B T)^{-1}$ , with  $k_B$  denoting the Boltzmann constant and  $T$  the absolute temperature. In this equation, we consider that species 1 is that with the larger surface tension of the two, and  $c$  is the concentration of species 2. The parameter  $a^2$  is referred to as the mean surface area per molecule. In a case where  $\sigma_1$  and  $\sigma_2$  are markedly different ( $\sigma_1$  sufficiently larger than  $\sigma_2$ ), a semi-empirical equation that apparently goes back to Szyszkowsky [5,6] reads

$$\frac{\sigma(c)}{\sigma_1} = 1 - D \ln \left( 1 + \frac{c}{A} \right), \quad (2)$$

where  $A$  and  $D$  are two constants characterising the mixture, while  $c$  denotes the concentration of the species with the smaller surface tension. It is also relevant to note

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the work of De Conick *et al.* [7]. These authors display an equation (their Equation 5.14) having a strong resemblance to Szyszkowsky's Equation (2) above. Very recently, Dobrovoly [8] has presented a statistical mechanical model for the surface tension of binary mixtures, which he was able to solve exactly. In particular, Dobrovoly obtains an explicit, though somewhat complex, expression linking the surface tension  $\sigma(c)$  of the mixture to those of its components, for a specific concentration  $c$ . The theory of De Conick *et al.* [7]. has some relation, via lattice-gas statistical mechanical models, to the study of Dobrovoly [8].

Some liquid alloys show deviations from the ideal behaviour, for instance, an enhanced decrease of  $\sigma(c)$  as the concentration of the second metal increases. This is the case for the liquid Ag–Sn alloy [1]. The deviation has been explained as due to an enhancement of the concentration of Sn at the surface of the alloy due to the lower surface tension of this metal [1]. Other specific alloys show more complex features. One of those is Fe–B [9,10].

A schematic equilibrium phase diagram of the Fe–B system [11] is given in Figure 1. The melting temperatures of the pure elements are  $T_m(\text{Fe})=1823\text{ K}$  and  $T_m(\text{B})=2360\text{ K}$ , respectively [12]. There is an intermetallic compound, Fe–B, with a melting temperature  $T_m(\text{Fe–B})=1863\text{ K}$ , and a deep eutectic depression at 17 atomic % B with an eutectic temperature of 1450 K. The surface tension of liquid Fe at its melting temperature is large [13],  $\sigma(\text{Fe})=1830\text{ Nm}^{-1}$ , and the surface tension of liquid boron at its melting temperature [14,15],  $\sigma(\text{B})=1060\text{ Nm}^{-1}$ , is nearly one-half of that for liquid Fe. The surface tension of this liquid alloy has been measured by Tomut *et al.* [9]. as a function of the boron concentration at three temperatures,  $T=1623$ ,

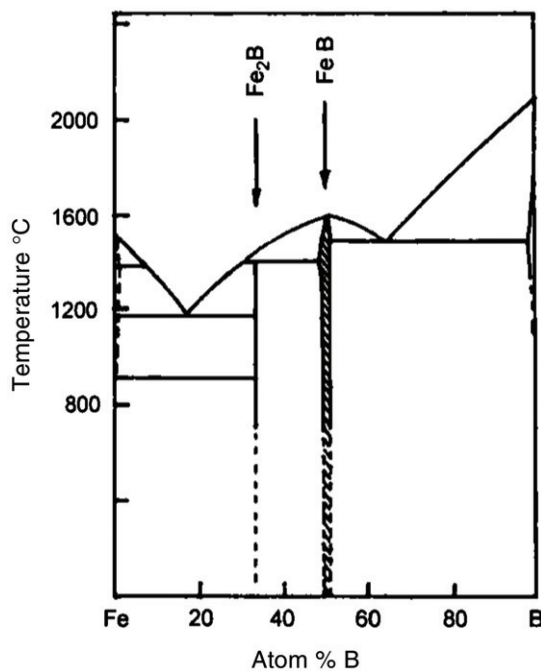


Figure 1. Schematic phase diagram of the Fe–B alloy. Redrawn from Moffat [11].

1723 and 1773 K. At those three temperatures the alloy is liquid only for a restricted range of compositions inside the eutectic depression. The measurements covered the concentration range from 15 to 25 atomic % B for the lowest of these temperatures, and from 15 to 34 atomic % B for the other two temperatures. A pronounced deviation from the normal behaviour was found: a minimum of  $\sigma(c)$  at about 17 atomic % B and a maximum around 24%.

None of the above treatments, despite their very varied degrees of sophistication, is sufficiently rich to allow for an interpretation of the surface tension of liquid Fe–B alloys. As starting point, let us consider the relatively simple semi-empirical Equation (2). One immediately finds the derivative  $d\sigma/dc$  as satisfying:

$$\frac{1}{\sigma_1} \frac{d\sigma}{dc} = -\frac{D}{A+c}. \quad (3)$$

But putting  $c=1$  in Equation (2) yields

$$\frac{\sigma_2}{\sigma_1} = 1 - D \ln\left(1 + \frac{1}{A}\right), \quad (4)$$

and combining Equations (3) and (4), one finds

$$\frac{d\sigma}{dc} = \frac{\sigma_2 - \sigma_1}{(A+c) \ln(1 + 1/A)}. \quad (5)$$

This slope is never zero; that is, the model does not allow for maxima and minima of  $\sigma(c)$  at intermediate concentrations. A similar conclusion is obtained from Equation (1), which yields

$$\beta a^2 \frac{d\sigma}{dc} = \frac{\exp(-\beta a^2 \sigma_2) - \exp(-\beta a^2 \sigma_1)}{(1-c) \exp(-\beta a^2 \sigma_1) + c \exp(-\beta a^2 \sigma_2)}. \quad (6)$$

Let us now consider the treatment of  $\sigma(c)$  in liquid binary mixtures by Bhatia and March [16]. Their treatment involves atomic size difference effects and the concentration fluctuations  $S_{cc}(0)$  in the mixture. This latter quantity, in turn, is related to the Gibbs energy,  $G$ , by [17]

$$S_{cc}(0) = \frac{Nk_B T}{(\partial^2 G / \partial c^2)_{T,p,N}}, \quad (7)$$

where  $N$  is the total number of atoms in the volume  $V$  under consideration, and  $p$  is the pressure. As an illustrative example of Equation (7), for the so-called class of regular solutions  $S_{cc}(0)$  has the form

$$S_{cc}(0) = \frac{c(1-c)}{1 + 2c(1-c)w/k_B T}, \quad (8)$$

where  $w$  is an interchange energy such that if we start, for example, with two pure metals  $M_1$  and  $M_2$  and exchange an interior  $M_1$  atom with an interior  $M_2$  atom, the total decrease in the energy of the metals is  $2w$ . For our present study it is important to note, quite generally, that  $S_{cc}(0)$  varies as  $c$  near  $c=0$ , and as  $(1-c)$  near  $c=1$ , as is already true for the regular solution form of Equation (8).

The phenomenological treatment of Cahn and Hilliard [18] for the surface tension of a pure liquid relates the product  $K_T\sigma$  of the isothermal compressibility  $K_T$  and the surface tension  $\sigma$ , to the thickness  $l$  of the liquid surface. The length  $l$  turns out for a whole variety of liquids near the triple point to be  $\approx 1 \text{ \AA}$ . The Cahn–Hilliard approach was subsequently generalized by Bhatia and March [16] to liquid binary alloys to yield

$$\sigma(c)K_T = l(c) \left( 1 + \frac{\delta^2 S_{cc}(0)}{nk_B T K_T} \right)^{-1}, \tag{9}$$

that is

$$\sigma(c) = l(c) \frac{nk_B T}{nk_B T K_T + \delta^2 S_{cc}(0)}. \tag{10}$$

Here  $n$  is the number density,  $n = N/V$ ,  $K_T(c)$  is the alloy compressibility and  $l(c)$  is a measure of the thickness of the liquid alloy surface. The important size difference factor  $\delta$  is given by

$$\delta = \frac{1}{V} \left( \frac{\partial V}{\partial c} \right)_{T,p,N} = \frac{V_1 - V_2}{cV_1 + (1-c)V_2}, \tag{11}$$

where  $V_1$  and  $V_2$  denote the partial molar volumes of the two species in the alloy. Though heuristic in nature, rather than based fundamentally on solvable statistical mechanical models, we shall confront now the predictions of Equation (10) with those of other models referred to above.

A difference between this result and the equations for the surface tension of mixtures mentioned at the beginning of this work is that Equation (10) allows for more drastic variations of the surface tension of the alloy as a function of composition. Denoting the quantity  $nk_B T K_T$  appearing in Equation (10) by  $\Theta$ , it is a simple matter to rearrange that equation to read

$$(\Theta + \delta^2 S_{cc}(0))\sigma(c) = k_B T n l(c). \tag{12}$$

Taking the derivative of Equation (12) with respect to the concentration  $c$ , and then putting  $\partial\sigma/\partial c = 0$  to estimate at maxima and minima ( $m$ ) with concentrations  $c_m$  say, the values of the surface tension  $\sigma(c) = \sigma_m$ , one finds

$$\sigma_m = \frac{k_B T (\partial(nl)/\partial c)_{c_m}}{((\partial\Theta/\partial c) + (\partial S_{cc}(0)/\partial c)\delta^2 - 2S_{cc}(0)\delta^3)_{c_m}}. \tag{13}$$

In reaching Equation (13), use has been made of Equation (11) to determine  $\partial\delta/\partial c$ . One binary liquid alloy to which Equation (13) should apply is the Fe–B system, and some qualitative ideas can be offered using the experimental information. The only magnitude appearing on the right hand side of Equation (10) which is expected to change drastically with concentration  $c$  is  $S_{cc}(0)$ . Then, a pronounced minimum of  $S_{cc}(0)$  would lead to a maximum of  $\sigma$ . Minima of  $S_{cc}(0)$  are associated to the occurrence of compositions where the interaction between the two components of the liquid alloy is specially attractive [19–22] and may have a significant degree of chemical short-range order. Those concentrations occur near the compositions corresponding to solid stoichiometric compounds. In a similar way, maxima of  $S_{cc}(0)$  will lead to minima of  $\sigma(c)$ . The phase diagram of the Fe–B alloy in Figure 1 shows a eutectic point at  $c = 17\%$  B and ordered

solid compounds at concentrations of 33.3 and 50% B. The measured maximum of  $\sigma(c)$  in the liquid Fe–B alloy occurs around 24 atomic % B for temperatures of 1773 and 1723 K, and at higher B concentrations for the lowest temperature in the experiment [9], 1623 K. The minimum of  $\sigma(c)$  occurs at 17 atomic % B. Those features correlate well with the phase diagram of the alloy, that is, the minimum of  $\sigma(c)$  occurs at the concentration of the eutectic, and the maximum is in the composition region of the intermetallic compounds. Unfortunately, to date, we do not have a tested model for the concentration fluctuations  $S_{cc}(0)$  across the phase diagram of Fe–B that would allow the application of Equation (13) to calculate the maximum and the minimum of  $\sigma(c)$ , but the arguments given above make clear the origin of the strong variation of  $\sigma(c)$  with concentration in the Fe–B alloy.

In summary, the usual models for the surface tension of liquid binary alloys do not explain the exceptional features, maxima and minima at intermediate concentrations, displayed by some complex alloys like Fe–B. We then propose that a model involving the concentration fluctuations in the liquid alloy, related in turn to the second derivative of the Gibbs free energy with concentration, contains the proper ingredients to account for those features, and we report a qualitative analysis that supports the proposal.

### Acknowledgements

This work was supported by MCYT of Spain (Grant MAT2005-60544-C03-01) and Junta de Castilla y Leon (Grant VA039A05). N.H.M. wishes to acknowledge the generous hospitality of L.M. Nieto and J.A.A. during visits to the University of Valladolid. N.H.M. was also partially supported at the University of Antwerp by FWO-Vlaanderen project number G.0425.05.

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