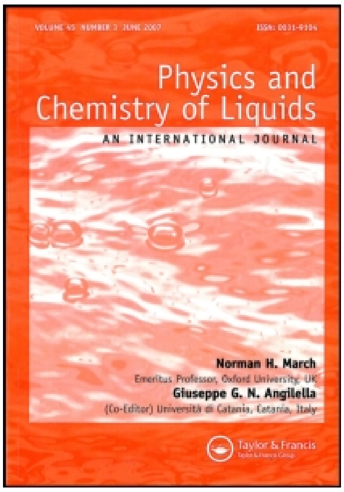

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Behavior of the Surface Tension and the Viscosity in the Eutecticregion of the Liquid Feb alloy

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BEHAVIOR OF THE SURFACE TENSION AND THE VISCOSITY IN THE EUTECTIC REGION OF THE LIQUID FeB ALLOY

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Thermodynamic and transport properties of pure liquid metals show interesting correlations near the melting temperature. This is well known for the case of the surface tension σ and the shear viscosity η. In this paper we investigate the possible extension of these correlations to binary alloys, taking the FeB alloy as a case study. Based on literature data we analyze the variation of σ and η as a function of temperature and concentration in a deep eutectic region of the phase diagram of this alloy, as well as the possible correlations between those two quantities. Substantial differences with respect to the behavior in pure metals are found.

Keywords: Surface tension; Viscosity; Metallic alloy

1. BACKGROUND AND OUTLINE

Studies of a relationship between the surface tension σ of pure liquid metals and bulk properties go back some decades. Thus, following ideas of Frenkel [1], the existence of the useful relationship

$$\sigma K_T = L \tag{1}$$

where K_T is the isothermal compressibility and L is a rather constant “characteristic” length, was stressed at the melting temperature T_m by Egelstaff and Widom [2], following phenomenological work by Cahn

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and Hilliard [3]. The present writers [4, 5] showed that L varied, but only modestly, between chemically similar groups of metals, but was generally about one third of an Angstrom. The generalization of Eq. (1), which will be taken up in Section 2 below, was effected to apply to liquid binary metallic alloys by Bhatia and March [6], their specific focus being surface segregation.

Somewhat later, various workers, and notably Egry [7, 8] have stressed the similarity between the Fowler formula [9] for the surface tension of a one-component liquid assumed to be characterized by a pair potential model and a corresponding formula by Born and Green [10] for the shear viscosity η. Egry introduced, in particular, the dimensionless ratio for a pure liquid metal

$$Q = \frac{16}{15} \frac{\sigma}{\eta v_{th}}. \tag{2}$$

Here v_{th} is the thermal velocity, defined as $v_{th} = (k_B T/m)^{1/2}$ where m is the ionic mass. He showed that Q had a value near to unity for the transition and noble metals at the melting temperature T_m. Deviations from a constant value are, however, non negligible and for the particular case of Fe, of interest for the present paper, $Q_{Fe} = 0.82$. Subsequently the present authors [11] have examined the choice that v_{th} in Eq. (2) is replaced by the velocity of sound: the quality of the correlation for a substantial number of pure liquid metals at T_m was somewhat improved.

In the present investigation the possibility of effecting generalizations of Eqs. (1) and (2) to liquid binary metallic alloys is the focal point. Thus in Section 2 and for a specific binary alloy for which surface tension data is available, namely Fe-B [12], the Bhatia-March [6] phenomenological formula for σ as a function of concentration is considered in relation to the phase diagram of this eutectic alloy. Then in Section 3 a generalization of Q in Eq. (2) is examined across the concentration range of this binary alloy. Section 4 constitutes a summary plus some proposals for further work.

2. SURFACE TENSION OF THE LIQUID Fe-B ALLOY

A schematic equilibrium phase diagram of the Fe-B system [13] is given in Figure 1. Features relevant to our purposes are, first of all, the

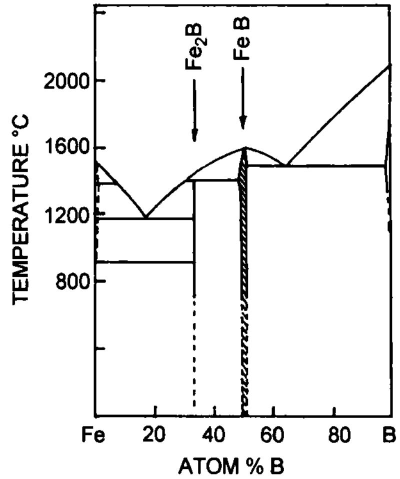

FIGURE 1 Schematic phase diagram of the Fe-B alloy. Redrawn from Moffat [13].

melting temperatures of the pure elements, $T_m(Fe) = 1823\,K$ and $T_m(B) = 2360\,K$ [14] respectively. The solid solubilities at both composition ends of the phase diagram, that is near pure Fe and pure B, are very small. There is an intermetallic compound, FeB, with a melting temperature $T_m(FeB) = 1863\,K$, and a deep eutectic depression midway between this compound and the pure Fe end. More precisely, the eutectic point is characterized by an eutectic composition of 17 at % B and a eutectic temperature of 1450 K. The surface tension of liquid Fe at its melting temperature is large [15], $\sigma(Fe) = 1830\,N\,m^{-1}$. On the other hand liquid Boron has a rather low surface tension at its melting temperature [16, 17], $\sigma(B) = 1060\,N\,m^{-1}$, that is nearly one half of that for liquid Fe. For this reason one could expect that, at constant temperature, the surface tension of the liquid $Fe_{1-c}B_c$ alloy would decrease with respect to the large value for pure Fe as the concentration of Boron is increased. The surface tension of this liquid alloy has been measured by Tomut *et al.* [12]. These authors presented surface tension isotherms at three temperatures, $T = 1623$, 1723 and 1773 K, as a function of the Boron concentration c. The phase diagram indicates that at these three temperatures the alloy is liquid only for a restricted range of compositions inside the eutectic valley. Indeed, the measurements cover the concentration field from 15 to 25 at % B for the lowest of these temperatures, and from 15 to 34 at % B for the other two temperatures. Roughly speaking, the measurements display the expected decreasing behavior of the surface tension as the Boron concentration is increased. However, Tomut *et al.* [12] discovered a common feature that deviates from the expected behavior of the surface tension curves: those three curves show a minimum at the eutectic composition.

The minimum found by Tomut *et al.*, can be qualitatively explained by the phenomenology of Bhatia and March [6]. The result of Bhatia and March for the concentration dependence of the surface tension generalizes Eq. (1) to read

$$\sigma K_T = \frac{L}{1 + (\delta^2 S_{cc}(0)/n k_B T\, K_T)} \tag{3}$$

where σ and K_T now refer to the alloy. Here n is the number density of the alloy, δ is a size factor

$$\delta = \frac{V_1 - V_2}{cV_1 + (1 - c)V_2} \tag{4}$$

written in terms of the atomic concentrations and the partial molar volumes of the two components, and $S_{cc}(0)$ represents the concentration fluctuations. In turn $S_{cc}(0)$ is related to the Gibbs free energy G(c) of the alloy through

$$S_{cc}(0) = \frac{n k_B T}{V(d^2G/dc^2)} \tag{5}$$

where V is the molar volume. *Via* Eq. (3), there is a route to estimate σ as a function of concentration

$$\sigma(c) = \frac{L}{K_T(1 + (\delta^2 S_{cc}(0)/n K_B T\, K_T))}. \tag{6}$$

However, besides knowledge of $S_{cc}(0)$, one requires the isothermal compressibility K_T as a function of concentration c as well as knowledge of the size factor δ. According to Eq. (4), the size factor changes smoothly with Boron concentration and the same is expected for the compressibility K_T. On the other hand it is well known that in those liquids with a tendency to short range heteroatomic association (compound-forming liquids) the concentration fluctuations $S_{cc}(0)$ have a non trivial behavior, showing a substantial negative deviation from the simple form $S_{cc}(0) = c(1-c)$, valid for an ideal liquid mixture. That deviation is such that the function $S_{cc}(0)$ has a sharp minimum, with a value near zero, precisely at the stoichiometric composition of the compound. Then the shape of the $S_{cc}(0)$ curve as a function of concentration is that of a minimum bounded by maxima both on its left and right sides. Plots of curves showing the stated behavior of $S_{cc}(0)$ in compound forming liquid alloys have been given, for instance, by March [18] and by Gallego *et al.* [19] for Mg-Bi and Li-Pb alloys respectively. Applying these ideas to the FeB alloy, we first notice that the alloy has a high melting compound, FeB, responsible for the eutectic valley centered at 17 at % Boron. This compound induces a sharp minimum of $S_{cc}(0)$ at $c = 0.5$, and consequently a local maximum of $S_{cc}(0)$ in the region where Boron is the minority component, that is in the region of the eutectic. Since $S_{cc}(0)$ is in the denominator in Eq. (6), the maximum of $S_{cc}(0)$ at the eutectic composition leads to a minimum of $\sigma(c)$: that is precisely the feature observed in the measurements of Tomut *et al.* [12]. From Eq. (3) one can notice that for the effect of the concentration fluctuations on σ to be significant, a substantial size mismatch δ is required, otherwise the term $(\delta^2 S_{cc}(0)/n\, k_BT\, K_T)$ will be very small. This condition is fulfilled in the FeB alloy, where the atomic volume of Fe is substantially greater than that of Boron.

3. VISCOSITY AND THE RELATION BETWEEN TRANSPORT AND THERMODYNAMIC PROPERTIES

In the same paper Tomut *et al.*, have measured the viscosity of the alloy as a function of Boron concentration in the same range of temperatures and concentrations as the measurements of the surface tension. The viscosity isotherms also display minima centered at the eutectic concentration. From early experimental work reviewed by Wilson [17] one expects a minimum of η at the eutectics (this feature will be discussed below) and also a maximum at those compositions consistent with formation of heteroatomic complexes in the alloy. The findings of Tomut *et al.*, are consistent with those expectations.

An interesting difference between the behaviour of the surface tension of the alloy on one hand and the viscosity on the other seen in

Tomut's results is that while $\sigma(c)$ varies by no more that 30% across an isotherm, $\eta(c)$ may vary by up to a factor of 4. This dissimilarity provides motivation to study the dimensionless ratio Q defined in Eq. (2) above, and so far analyzed only for pure metals. Since the data for σ and η at our disposal is rather restricted we analyze Q along isotherms, as a function of Boron concentration. Table I gives the results for $\sigma(c)$ and $\eta(c)$, and the corresponding values of Q(c) at several compositions for T = 1773 K, 1623 K, 1573 K and 1523 K, respectively. The values of $\sigma(c)$ and $\eta(c)$ have been directly estimated from the plots given by Tomut *et al.* In forming $v_{th} = (k_BT/m)^{1/2}$ for the alloy, the mass m(c) has been defined as the concentration average of the masses of Fe and B (another alternative could be averaging directly the thermal velocities of the two components of the alloy but the results will be similar).

Some salient features are observed in the Table. At fixed concentration c the values of Q decrease with decreasing temperature of the liquid alloy. On the other hand, at fixed T the values of Q(c) vary substantially with Boron concentration across the isotherm. Overall, Q(c) for the alloys is in all cases smaller than 0.82, which is the value of Q_{Fe} at T_m(Fe). We now consider the first observation, that is

TABLE I Surface tension σ, viscosity η, ratio σ/η, and dimensionless ratio Q (defined in Eq. (2)), for liquid $Fe_{1-c}B_c$ alloys at several temperatures. Data for σ and η read from figures in Tomut *et al.* [12]

c	$\sigma(Nm^{-1})$	$\eta(mPa\,s)$	σ/η	Q
T = 1523 K				
0.15	1.33	18.75	0.07	0.15
0.20	1.23	15.18	0.08	0.17
T = 1573 K				
0.15	1.33	6.25	0.21	0.44
0.20	1.26	12.20	0.10	0.21
T = 1623 K				
0.15	1.40	4.88	0.29	0.58
0.17	1.14	3.57	0.32	0.64
0.20	1.19	9.23	0.13	0.26
T = 1773 K				
0.15	1.26	3.57	0.35	0.69
0.17	0.91	2.68	0.34	0.65
0.20	1.14	4.76	0.24	0.46
0.25	1.20	12.80	0.09	0.17

the temperature effect. By collecting data for σ and η for temperatures other than the melting temperature, Egry [8] also investigated the validity of Eq. (2) for the pure noble metals and the transition metals Fe, Ni and Co in a finite temperature interval of 300 K centered on T_m of each individual metal. This means that the investigated temperature range includes the supercooled liquid. Our analysis of the data for Fe provided in Figure 2 of Egry's paper [8] shows that Q_{Fe} depends on T. In fact $Q_{Fe}(T)$ becomes closer to the ideal value of 1 as T increases above T_m; conversely $Q_{Fe}(T)$ becomes progressively smaller that 0.82 as T decreases below T_m, increasingly deviating from the ideal value of 1. All the temperatures in Table I, sampling the eutectic depression of the alloy, are below T_m(Fe). In fact, Boron plays the role of stabilizing the liquid below the melting temperature of the pure solvent [20], due to the entropy of mixing and a favorable Fe-B enthalpy of mixing. Then, the above mentioned feature in Egry's work justifies the small values of Q seen in Table I. The decrease of Q with decreasing temperature found for both pure metals and alloys has its origin in the different dependence of σ and η with T. It is generally accepted that in liquid metals σ changes linearly with T,

$$\sigma(T) = \sigma(T_m) + \frac{d\sigma}{dT}(T - T_m) \tag{7}$$

and since the derivative in Eq. (7) is negative, σ increases linearly below T_m. On the other hand it has also been proposed that η displays an exponential behavior

$$\eta(T) = \eta_0 \, e^{A/RT} \tag{8}$$

and also increases its magnitude on supercooling below T_m. But the different dependence on T shown by Eqs. (7) and (8) indicates that, on supercooling, the increase of η is more pronounced than the increase of σ and consequently one can expect that the ratio σ/η would diminish with increasing degree of supercooling. This is precisely what the Table shows. If we take a fixed concentration, for instance $c = 0.15$, the ratio σ/η takes values 0.35, 0.29, 0.21 and 0.07 for $T = 1773$, 1623, 1573 and 1523 respectively. The corresponding values of Q in the Table are 0.69, 0.58, 0.44 and 0.15, which show the increasing deviation from 1 as T deviates from T_m(Fe). A similar trend is observed if we take

$c = 0.20$. But it is worth recalling that Egry has challenged the general validity of Eqs. (7) and (8), and some of the measurements of σ in Tomut's paper for the FeB alloys (see, in particular, their Fig. 4) point in the same direction.

The trend of Q as a function of Boron concentration, at fixed temperature, is an overall decrease with increasing c, although the data at low temperatures ($T = 1523$ and 1623 K) hint to a possible weak maximum at the eutectic composition $c = 17$ at %. The overall decrease of Q(c) for increasing c reflects, in our view, the increasing proximity of the intermetallic compounds Fe_2B and FeB, with respective melting temperatures 1680 K and 1871 K. Near those compositions the tendency for association in the liquid alloy is strong, so atomic transport may become more difficult because of the formation of heavier diffusing units, the cluster complexes. A less speculative view, that leads to the same conclusion, is to consider the enhanced number of strong heteroatomic bonds that develop in the liquid as the composition approaches the ideal compound stoichiometry. Those strong bonds make atomic transport difficult. Consequently $\eta(c)$ is expected to increase steeply, a feature displayed in Figure 3 of Tomut's paper, or in our Table I for $T = 1773$ K, and this leads to the decrease of Q(c) for increasing c. As recalled above, the experimental $\sigma(c)$ and $\eta(c)$ isotherms present a minimum at the eutectic composition. That minimum is especially pronounced in the case of η at low temperatures (for instance at $T = 1523$). Since it is the variation of η that mainly controls the behavior of Q(c), the minimum of $\eta(c)$ induces the weak maximum of Q(c) at the eutectic composition.

4. SUMMARY

The measured variation with composition of the surface tension of liquid $Fe_{1-c}B_c$ alloys at constant temperature can be understood from the Bhatia-March phenomenology [6], given in Eq. (3), which highlights the prominent role of the concentration fluctuations $S_{cc}(0)$ across the phase diagram, and the size difference δ. Turning to the viscosity of the liquid alloy, the variation of this quantity with Boron concentration appears to reflect the formation of strong Fe-B bonds for compositions close to the stoichiometry of the solid compounds.

We have investigated the extension of the Egry [7, 8] factor Q to alloys, where the thermal velocity v_{th} in Eq. (2) has been generalized to include an average mass. What is quite clear is that Q now varies with temperature and concentration, so its utility for alloys is doubtful. A point that deserves further investigation is the precise variation of the viscosity at eutectics, and in particular the appearance of a minimum for this quantity.

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