



An innovative model for correlating surface tension, solubility parameters, molar volume and ratio of the coordination numbers of liquid metals, based on Stefan's rule



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ABSTRACT

Surface tension has direct applications in the field of material science, playing a key role in applications such as metal alloy formation, phase match/ separation, nanodispersion and organometallic synthesis for chemical industrial purposes. Although extensively used, the accurate surface tension of liquid metals is difficult to measure due to the high boiling point; it is therefore important to achieve theoretical or empirical methods for predicting it. Semi-empirical predictions based on the correlation between the surface and bulk thermodynamic properties of liquid metals are possible, such as linking surface tension to the heat of evaporation. Formerly, on the basis of a computer regression of a large database, Beerbower (1971) [3] showed a relationship between the Hildebrand solubility parameter, surface tension and molar volume, which applies for both organic molecules and metal liquids. More recently, Strechan et al. (2006) [10] introduced a relationship between the ratio of the coordination numbers, surface tension, molar volume and enthalpy of vaporization of organic molecules, using Stefan's rule as a physicochemical background. The present study introduces a novel semi-empirical relationship based on the correlation between the surface and bulk thermodynamic properties of liquid metals and the Hildebrand solubility parameter. The original inclusion of the ratio of the coordination numbers to Stefan's rule strengthens the relationship between the solubility parameters and the physical backgrounds they represent and enhances the computational accuracy of predicted liquid metals surface tension.

1. Introduction

Surface tension is believed to be due to the unbalanced forces of the surface atoms. For each surface atom, these unbalanced forces are a fraction of the total forces, therefore, higher latent heat is required for the fusion of a metal, the atom of which has stronger forces, and, thereby its liquid has higher surface tension [8].

The main cause of the surface tension of all liquids (and solids), whether metallic or not, is the same: the total surface energy is determined by the amount of energy required to bring the molecules or atoms (and electrons) from the bulk of the condensed phase to their free surface, while enlarging the surface area.

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high boiling point; it is therefore important to achieve theoretical or empirical methods for predicting it.

Semi-empirical predictions based on the correlation between the surface and bulk thermodynamic properties of liquid metals are possible, such as linking surface tension to the heat of evaporation. In addition, surface tension of pure substances may be evaluated from values of critical temperature using empirical equations [1].

Garai [4] proposed an atomic model for calculating the latent heat of vaporization of 45 periodic table elements. Using solely physicochemical parameters and a correlation coefficient, he calculated the latent heat of vaporization for monoatomic liquids with a high level of accuracy.

Recently, Ruvireta et al. [9] proposed that methods based on Stefan's formula are only qualitatively suited. However, the authors show in the present study that an updating of the method can give results with a high degree of accuracy and yet be of simple application.

Formerly, on the basis of a computer regression of a large database,

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Beerbower [3] showed a relationship between the cohesive energy density (δ_T^2), and surface tension and molar volume (surface tension per molar volume^{1/3}). Such a relationship between the cohesive energy density and the Gordon parameter ($\sigma_L/V^{1/3}$) applies for molten metals and organic liquids.

More recently, Strechan et al. [10] introduced a relationship between the ratio of the coordination numbers, surface tension, molar volume and enthalpy of vaporization (ΔH_{vap}) of organic molecules, using Stefan's rule as a physicochemical background. Closely related to the cited physicochemical parameters, the cohesive energy density (C.E.D) is derived from the heat of vaporization (ΔH_{vap}) and is also the basis of the Hildebrand solubility parameters.

The term *solubility parameter* was first used by Hildebrand in 1949 [7] and is defined as the square root of the total cohesive energy density ($CED \equiv E/V$) [6]:

$$\delta_T = (E/V)^{1/2} \quad (1)$$

where V is the molar volume of the pure liquid and E is its energy of vaporization.

As cited, the solubility parameter is a thermodynamic quantity related to the energy of cohesion in liquids. When the energy of vaporization data is unavailable, Hildebrand and Scott [6] suggest a number of more-or-less empirical methods for determination of the solubility parameter. Among these is the following relationship:

$$\delta_T = 4.1 \left(\frac{\sigma_L}{V^{1/3}} \right)^{0.43} \quad (2)$$

where σ_L is the liquid surface tension measured in dyn.cm^{-2} ($= \text{erg.cm}^{-2}$), and the molar volume is measured in $10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$. This equation is rather unsatisfactory as it is dimensionally inhomogeneous in the exponent, although it gives satisfactory values of the solubility parameter in many cases [2].

Subsequently, on the basis of a computer regression of a larger database than was available to Hildebrand and Scott [6], Beerbower [3] showed that the relationship is more correctly expressed as:

$$\delta_T = 3.741 \left(\frac{\sigma_L}{V^{1/3}} \right)^{1/2} \quad (3)$$

or, in terms of the liquid surface tension:

$$\sigma_L = \frac{\delta_T^2 V^{1/3}}{13.992} \quad (4)$$

Eqs. (3) and (4) are dimensionally homogeneous because the energy density can be calculated as erg.cm^{-3} , the same unit as the Gordon parameter ($\sigma_L/V^{1/3}$). The Hildebrand solubility parameter is the square root of the cohesive energy density and can also be expressed as the square root of pascals or the square root of calories per cubic centimeter ($1 \text{ erg/cm}^3 = 23.9 \times 10^{-9} \text{ cal/cm}^3 = 10^{-1} \text{ Pa}$) [Eq. (1)].

Another relationship between physicochemical parameters and surface tension is Stefan's Rule. According to Hildebrand and Scott [6], the surface tension of liquids can be predicted from Stefan's Rule:

$$\sigma_L = 0.13 \Delta H_{vap} V^{2/3} \quad (5)$$

where σ_L = surface tension (mN.m^{-1}), ΔH_{vap} = heat of vaporization (kJ.mol^{-1}); V = molar volume ($10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$).

Stefan's rule, which establishes the dependence between the enthalpy of vaporization (ΔH_{vap}), the surface tension (σ_L), the molar mass of a substance (M) and its density (ρ), can be further discriminated in this equation [10]:

$$\sigma_L = (Z_S/Z) \left[\frac{\Delta H_{vap} \rho^{2/3}}{M^{2/3} N_A^{1/3}} \right] \quad (6)$$

where ΔH_{vap} = enthalpy of vaporization (kJ.mol^{-1}), σ_L = surface tension (mN.m^{-1}), Z_S and Z are the surface and bulk coordination numbers for molecules of the liquid, respectively, M = molar mass (g),

ρ = density (g.cm^{-3}), and N_A = Avogadro number.

Strechan et al. [10] calculated the ratio of the coordination numbers ($\frac{Z_S}{Z}$) and found them ranging between 0.0559 and 0.1784 for different liquid molecules. It is worth noting that the average value ($\frac{Z_S}{Z} \approx 0.13$) approximates the coordination numbers ratio to the Stefan constant [Eq. (5)].

The corrected Hildebrand solubility parameter [Eq. (1)] is defined as below:

$$\delta_T = \left(\frac{\Delta H_{vap} - RT}{V} \right)^{1/2} \quad (7)$$

where δ_T is the Hildebrand solubility parameter ($\text{mPa}^{1/2}$), ΔH_{vap} = enthalpy of vaporization (kJ.mol^{-1}). R (universal gas constant) = 8.314 and RT is the temperature correction factor ($\text{J.mol}^{-1} \cdot \text{K}^{-1} \cdot \text{mol}$).

Based on Eqs. (7) and (13), the following equation is proposed (see Appendix for the equation deduction):

$$\delta_T = 2.806 \left(\frac{Z}{Z_S} \frac{\sigma_L}{V^{1/3}} \right)^{1/2} \quad (8)$$

where $\left(\frac{Z}{Z_S} \right)$ is the reciprocal of the ratio of the coordination numbers, δ_T is the solubility parameter ($\text{mPa}^{1/2}$), σ_L = surface tension (mN.m^{-1}) and 2.806 is an empirical constant.

Rearranging the terms in Eq. (8), the liquid surface tension (σ_L) can be estimated using the following expression:

$$\sigma_L = 0.127 \left(\frac{Z_S}{Z} \right) \delta_T^2 V^{1/3} \quad (9)$$

The present study introduces a novel semi-empirical relationship based on the correlation between the surface and bulk thermodynamic properties of liquid metals and the Hildebrand solubility parameter (δ_T). The original inclusion of the ratio of the coordination numbers to Stefan's rule strengthens the relationship between the solubility parameters and the physical backgrounds they represent and enhances the computational accuracy of liquid metal surface tension.

2. Methodology

The physicochemical parameters molar volume (V), boiling point (T_b , K), enthalpy of vaporization (ΔH_{vap} at T_b or ΔH_{vap} , kJ.mol^{-1}) and surface tension (σ_L) were taken from published data from Agra and Ayyad [1]; the $\left(\frac{Z_S}{Z} \right)$ parameter, calculated δ_T and predicted surface tension (σ_L) were calculated using various equations. The data is shown in Table 1.

The ratio of the coordination numbers $\left(\frac{Z_S}{Z} \right)$ parameter is calculated using the method of Strechan et al. [10], through the following equation:

$$\frac{Z_S}{Z} = \frac{\sigma_L V^{2/3} N_A^{1/3}}{\Delta H_{vap}} \quad (10)$$

The liquid surface tension (σ_L) can be calculated using a simplification of Eq. (9) without the ratio of the coordination numbers through the following expression:

$$\sigma_L = 0.0146 V^{1/3} \delta_T^2 \quad (11)$$

Strechan et al. [10] also proposed a method for adjusting the enthalpy of vaporization within different chemical groups using the a and b coefficients. The a and b coefficients result from a performed optimization when correlating the experimental enthalpy of vaporization and the parameter predict through the use of the surface tension per volume product (surface tension per molar volume^{2/3}), in accordance with Eq. (12):¹

¹ The result is divided by 1000 to convert from J.mol^{-1} to kJ.mol^{-1} .

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