

# Surface tension regularity of non-polar, polar, and weak electrolyte liquid hydrocarbons

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Received 2 April 2004; received in revised form 12 May 2005; accepted 13 May 2005

## Abstract

The correlation of reduced surface tension  $\sigma_{sc}^*$  versus reduced temperature  $T_{sc}^*$  which produces family of linear curves is investigated for universality. Each curve is characterized by the reduced temperature index  $T_{index}^*$  which is included in  $T_{sc}^*$ . The correlation is based on phenomenological scaling law and consideration of law of corresponding states. The reduced temperature  $T_{sc}^*$ , scaled distance from the boiling temperature  $T_b$ , has the practical advantage of being independent of critical temperature. The correlation is highly accurate when applied to 10 classes of non-polar, slightly polar, polar, and weak electrolyte liquid hydrocarbons. The slopes of linear curves of each class of liquids at given  $T_{index}^*$ 's are rather constant and a universal regularity among all liquid is very likely, however small differences identify three classes of non-polar, slightly polar, and polar plus weak electrolytes. Consideration of the pervious application to molten alkali halides, molten salts, and molten metals, and considering that the reduced surface entropy  $S^{**} = (\partial\sigma_{sc}^*/\partial T_{sc}^*)$  is rather constant for all liquid tested, strengthen the idea that  $\sigma_{sc}^*-T_{sc}^*$  correlation is likely universal.

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**Keywords:** Law of corresponding states; Liquid hydrocarbons; Molten metals; Molten salts; Surface tension; Correlation for surface tension; Weak electrolytes

## 1. Introduction

Surface tension is an important property where wetting, penetration, foaming, or droplet formation of a liquid is considered, and where environmental profile is encountered [1,2]. Values of gas–liquid interfacial tension are used in studying of liquid–liquid and liquid–solid interfaces, as well as the design of fractionators, absorbers, separators, two-phase pipeline, and in reservoir design calculations [1]. It is also a parameter required for drug formulation and drug product design [3,4]. Surface tension, among other physical and thermodynamic properties of liquids, is a basis for practical and theoretical modeling of the liquid state of matters [5]. It varies with temperature linearly and vanishes non-linearly close to critical point  $T_c$ , where the interface fades out. Although surface tension can be measured accurately by experimental methods, it has been

correlated with many physical properties, for both prediction and validation of theories of interface. Relationship involving the melting point, molar volume, and heat of vaporization are the most meaningful [6]. For best application correlations based on the law of corresponding states have been established and thus, the applicability becomes universal [7].

The correlation of surface tension with temperature, given by van der Waals and then developed by Guggenheim [7], as  $\sigma = \sigma_o(1 - T_r)^m$ , requires knowledge of the substance-dependent constant  $\sigma_o$ , and the critical temperature  $T_c$ , where  $\sigma$  is the surface tension,  $T$  the absolute temperature, and the reduced temperature  $T_r = T/T_c$ . The constant  $m$  has universality and its reported values are in the range 1.16 [8], which are different from the theoretical values of 1.26 [9]. Further works have progressed to express  $\sigma_o$  in terms of  $T_c$ , the critical pressure  $P_c$ , and a substance-dependent constant in terms of boiling temperature [10].

Based on phenomenological scaling, Lielmezs and Herrick [8] have presented a correlation as a single linear

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curve in the form of corresponding states, applicable to a wide range of atomic, spherical, alkanes, and slightly polar organic liquids. This correlation and its modified form [5] have been applied to molten metals [5,11], while requiring  $T_c$  and predicts surface tension within 15% for molten metals [11], and within 14% of experimental values of atomic and molecular normal fluids [8]. This and similar correlations result in the corresponding states of surface tension in terms of temperature scaled distance from  $T_c$ . One of the present author has presented a reasonably accurate modified form of the above correlation in which surface tension is given as function of temperature scaled distance from boiling temperature [5], and thus, it has found practical application for the fact that it is independent of critical temperature. It is applicable to molten alkali metals over a wide range of temperature with maximum average deviation of 2.43% [5], and to molten alkali halides with maximum average deviation of 7.5% [6].

In the present study, we investigate the features of  $\sigma_{sc}^* - T_{sc}^*$  correlation for universality by considering different classes of liquid hydrocarbons from non-polar to slightly polar and weak electrolytes. These hydrocarbons are of importance as solvent and as the building block of industrial products, biochemical, and biological systems [12,13]. The results of this study and the previous results of application to important materials of engineering type are used to qualify the universality.

## 2. Surface tension regularity

Based on phenomenological scaling law [8], and consideration of law of corresponding states, relations have been presented for surface tension, which are mainly aimed to correlate surface tension in terms of physical properties of fluid bulk. The accuracy of these correlations has been noted by a number of applications to normal liquids [14], molten salts [15], and molten metals [16]. A reasonably accurate modified form of the above correlation in which the reduced surface tension  $\sigma^* = (\sigma/T)(\sigma_f/T_f)$  is given as function of reduced temperature  $T^* = [(T_b - T)/(T_b - T_f)](T_f/T)$  (scaled distance from boiling point) has been presented, where subscripts b and f stand for boiling and freezing points, respectively. It has found practical applications for the fact that it is independent of critical temperature. The correlation of  $\sigma^*$  with  $T^*$  results in a single curve from freezing point to boiling point. Following successful applications, it has been argued that since surface tension is a measure of intermolecular interaction potential should not have necessarily the same weighting as  $T$  which is a measure of thermal energy. Consistence with these theories, then we have found empirically a new regularity for the surface tension in which a family of linear functionals were produced by [6],

$$\sigma_{sc}^* = \left(\frac{\sigma}{\sigma_f}\right)^{n+1} \left(\frac{T_f}{T}\right) \quad (1)$$

as a function of

$$T_{sc}^* = \left(\frac{T_b - T}{T_b - T_f}\right) \left(\frac{T_f}{T}\right) \left(\frac{\sigma}{\sigma_f}\right)^n \quad (2)$$

where  $\sigma$  is the surface tension,  $n$  a constant value,  $T_f$  and  $\sigma_f$  the absolute temperature and surface tension at the freezing point, respectively, and  $T_b$  is the absolute temperature at the boiling point. The fact that correlation  $\sigma_{sc}^*$  with  $T_{sc}^*$  (is referred to as  $\sigma_{sc}^* - T_{sc}^*$ , hereafter) is independent of the critical temperature makes it of special interest for practical application. The first application to molten alkali halides indicates that  $\sigma_{sc}^* - T_{sc}^*$  is highly accurate, with linear correlation coefficient (LCC) between 0.9992 and 0.9998. Each curve of the family of curves is indexed by

$$T_{index}^* = \left[\frac{T_b - T}{T_b - T_f}\right] \quad (3)$$

involved in  $T_{sc}^*$ . In Eqs. (1) and (2),  $n$  is a constant equal to 4.0. With  $n=0$ ,  $\sigma_{sc}^* - T_{sc}^*$  is reduced to the previous  $\sigma^* - T^*$  correlation [5], in which no indexing was applicable and only a single curve is produced. When molten alkali halides are treated with  $\sigma^* - T^*$  correlation, a single linear curve with LCC=0.9906 is produced, below the limit for considering a curve satisfactorily linear. Therefore, for  $\sigma_{sc}^* - T_{sc}^*$ , the high accuracy is gained by including  $T_{index}^*$  in the definition of  $T_{sc}^*$  and thus, it is the key point for producing a quite accurate universal relationship. Since the form of  $T_{sc}^*$  is rather complex, it worth mentioning that  $T_{sc}^* = T_{sc}^*(T_{index}^*, \sigma; \sigma_f, n = 4.0)$  equally clarify the physical structure of  $T_{sc}^*$  as  $T_{sc}^* = T_{sc}^*(T, \sigma; T_f, \sigma_f, T_b, n = 4.0)$  does. However, the former has a special feature presented in particular, leading to simple procedure for the construction of  $\sigma_{sc}^* - T_{sc}^*$  correlation.

While the accuracy is excellent, the critical temperature is excluded and this makes  $\sigma_{sc}^* - T_{sc}^*$  preferential over the counterpart correlations. This is of practical interest for both prediction and validation of theory of interface when the organic liquids with high  $T_c$ , susceptible to decomposition at high  $T$ 's, are involved.

Empirically, we have found that the value 4.0 is an exact lower limit of  $n$  for molten alkali halides [6]. This has been the case for the subsequent reported applications [14–16], and a higher limit cannot be specified [6]. For  $n > 4.0$ , the linear behavior persists but the accuracy will be decreased, as indicated by decreasing LCC.

## 3. Results and discussion

The correlation  $\sigma_{sc}^* - T_{sc}^*$  has been applied to molten alkali halides [6], alkanes [14], molten salts [15], and molten metals [16]. (See the notes in Refs. [14] and [16].) In this study, we investigate to demonstrate its application as a universal correlation. To achieve this, we have selected 10 sets of organic liquid of different polarity. The liquids and their physical properties are listed in Table 1. The liquids involved are mainly long chain hydrocarbons and their

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