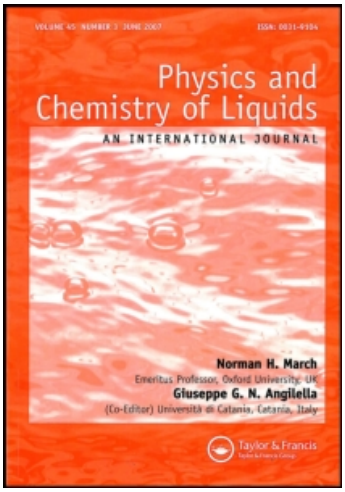

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Temperature Dependence of the Surface Tension of Alkali Metals: A Unified Correlation

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TEMPERATURE DEPENDENCE OF THE SURFACE TENSION OF ALKALI METALS: A UNIFIED CORRELATION

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In this work, new definitions of the normalized temperature and surface tension are proposed which result in a single plot for the surface tension of molten alkali metals. The functional dependence of the reduced surface tension on the reduced temperature can be adequately described by a straight line; the intercept and slope have been obtained using the linear regression approach. The method proposed herein predicts the values of surface tension at various temperatures with an average error of about 5%.

KEY WORDS: Alkali metals, surface tension, reduced temperature, reduced surface tension.

INTRODUCTION

In recent years, considerable interest has been shown in studying the variation of the surface tension with temperature in liquid metals. Such investigations have received impetus from both practical as well as theoretical considerations. From a practical viewpoint, a knowledge of the surface tension of molten metals is necessary to an understanding of a range of metallurgical processes such as those encountered in smelting and refining operation, gas absorption, nucleation and growth of gas bubbles and other nonmetallic inclusions, etc. On the other hand, the experimental values of the surface tension are needed to validate theories and models of the liquid state. Conversely, the usefulness of a model must be judged by its ability in yielding accurate and reliable values of the surface tension as a function of temperature. There is no question that considerable progress has been made in developing various models which purport to provide an adequate description of the structure of liquid metals but unfortunately it is not yet possible to have a completely theoretical basis for the estimation of the surface tension of molten metals. Most of the progress in this area therefore has been made through the use of empirical or semitheoretical formulations, and consequently, there is no scarcity of predictive expressions in the literature.

Numerous attempts have been made to correlate the surface tension of molten metals with a range of bulk physical properties including atomic volume and critical

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temperature[1], heat of vapourization[2], bulk coefficient of thermal expansion[3], internal pressure and plasma frequency[4,5], etc. Some of these developments[2–5] are restricted to the prediction of the surface tension at melting point whereas others[1] purport to be applicable over the complete temperature ranges. However, all such equations involve constants which vary from one metal to another, and none of the equations has proved to be completely successful. Informative and critical reviews of the theoretical as well as experimental developments in this area are available in the literature[6–8].

In recent years, there has been a renewed interest in the use of the principles of corresponding states for the prediction of physical properties of ordinary liquids as well as liquid metals. These have proved to be moderately successful in predicting viscosity and diffusivity of liquid metals[9,10]. In this paper, the applicability of the corresponding states principle is examined for predicting the surface tension of the five alkali metals. Based on semi-empirical considerations, a unified correlation for the surface tension of alkali metals is developed, and the resulting values of the surface tension of alkali metals have been compared with the corresponding experimental values over extensive ranges of temperature.

DEVELOPMENT OF THE PROPOSED CORRELATION

Based on the phenomenological scaling and renormalisation group theory considerations, Lielmezs and Herrick[11] introduced the following reduced state coordinates, namely, surface tension and temperature:

$$\sigma^* = \frac{\sigma/T}{\sigma_B/T_B} \tag{1}$$

$$T^* = \frac{(T_c/T) - 1}{(T_c/T_B) - 1} \tag{2}$$

Following the simple principle of corresponding states, Lielmezs and Herrick[11] argued that a unique relation must exist between σ^* and T^*. Indeed this assertion was borne out by scores of simple organic liquids over extensive temperature ranges.

Intuitively, one would expect that the reduced variables should also result in a single curve at least for alkali metals which belong to the same group of the periodic table and exhibit a great deal of structural similarity. However, a difficulty arises in employing the definitions of the reduced surface tension and temperature given in Eqs. (1) and (2) simply because the critical constants of metallic elements are not known as accurately as those of the ordinary liquids. Therefore, it is preferable to use the respective melting and boiling points as the two characteristic temperatures, and the reduced surface tension and temperature are re-defined as:

$$\sigma^* = \frac{\sigma/T}{\sigma_m/T_m} \tag{3}$$

$$T^* = \frac{(T_B/T) - 1}{(T_B/T_m) - 1} \tag{4}$$

Evidently, T^* takes on values between zero and one as the temperature decreases from boiling point to melting point whereas the reduced surface tension is always smaller than one.

Now, one would expect that the use of the reduced variables would result in a single curve for alkali metals. This expectation is confirmed in Figure 1 which shows a strong common $\sigma^* - T^*$ inter-relation for the five alkali metals encompassing the temperature range from their respective melting to boiling points. The experimental values of the surface tension as a function of temperature have been taken from the Smithell's Metal reference book[12]. Table 1 provides a brief summary of the ranges of data used herein. To describe the functional relationship shown in Figure 1, the following linear expression was introduced:

$$\sigma^* = AT^* + B \tag{5}$$

where A and B are two constants which have been evaluated using the method of linear regression as:

$$A = 0.81135; \qquad B = 0.1877$$

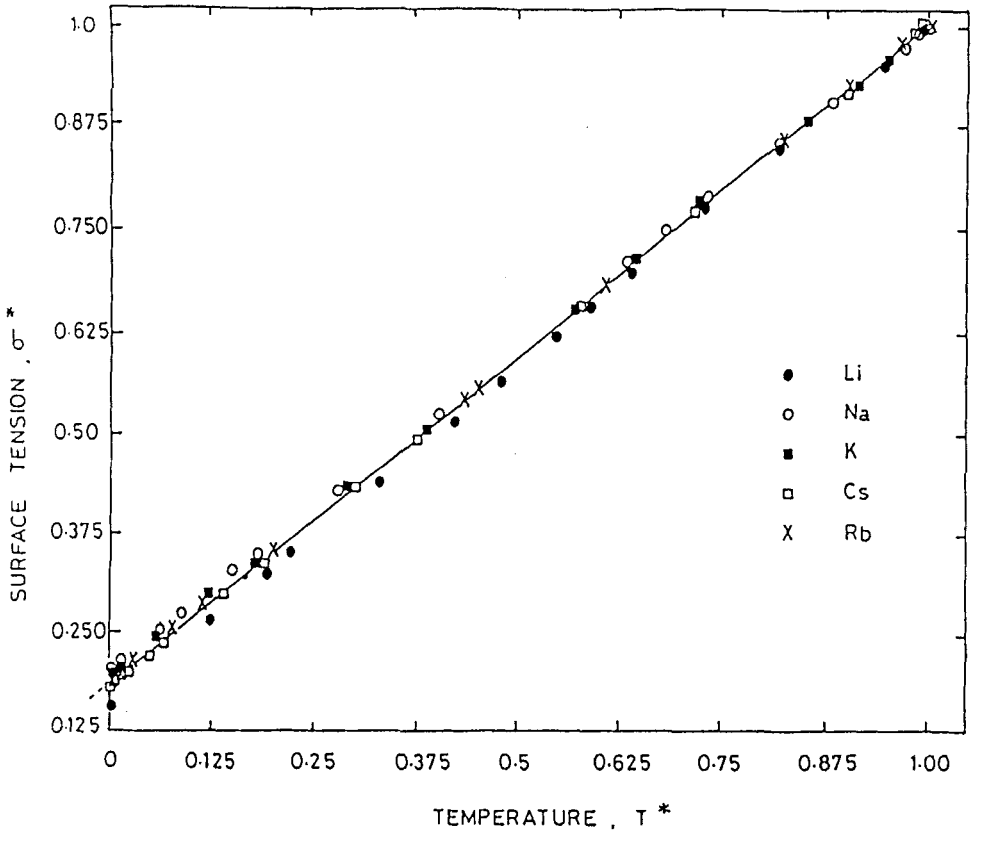

Figure 1 $\sigma^* - T^*$ relation for alkali metals.

Table 1 Characteristic constants of alkali metals used in this work (From Ref. 12).

Metal	*Melting Point* T_m, (K)	*Boiling Point* T_b, (K)	σ_m $(mN.m^{-1})$
Cesium	301.5	943	69
Lithium	454	1615	395
Potassium	336.2	1032	111
Rubidium	311.8	961	83
Sodium	370.8	1156	195

The regression coefficient is 0.9993 and the standard deviations of A and B are 0.013 and 0.006 respectively. The solid line drawn in Figure 1 represents the predictions of Eq. (5).

COMPARISON WITH EXPERIMENTAL RESULTS

Though Figure 1 itself is indicative of the excellent agreement between the experimental values of the surface tension and those calculated from Eq. (5), it is desirable and appropriate to present comparisons between the calculated and experimental values in terms of $\sigma - T$ variables rather than $\sigma^* - T^*$. A detailed statistical analysis of the data revealed that the agreement between the experimental and calculated (using Eq. (5)) values is excellent. The resulting average and maximum deviations are listed in Table 2. Bearing in mind the fact that the experimental determination of the surface tension entails an uncertainty of the order of 10–15% the correspondence between the predicted and actual values of σ is regarded to be satisfactory and acceptable.

Finally, before concluding the discussion, it is also appropriate to compare the experimental and calculated values of the slopes of $\sigma - T$ behaviour. Equation (5)

Table 2 Summary of results.

Metal	*Error in prediction of surface tension*		*Values of* $(d\sigma/dT)$ $(mN.m^{-1}.K^{-1})$	
	Average	*Maximum*	*Calculated from Eq. 5*	*Experimental*†
Cesium	1.75%	4.1%	−0.044	−0.047
Lithium	4.8%	11.4%	−0.134	−0.150
Potassium	1.72%	5.58%	−0.067	−0.063
Rubidium	0.9%	2.56%	−0.054	−0.052
Sodium	3.06%	9.3%	−0.099	−0.090

† From Ref. 12.

can be rearranged to obtain the slope of $\sigma - T$ data as follows:

$$-\frac{d\sigma}{dT} = \frac{0.81135\sigma_m}{(T_B - T_m)} - 0.1877\frac{\sigma_m}{T_m} \tag{6}$$

The experimental and calculated values of $(d\sigma/dT)$ are also included in Table 2 where it is seen that the two values are within $\pm 10\%$ of each other. Though, the values of the surface tension entail an uncertainty of the order of 10–15%, the reported values of $(d\sigma/dT)$ appear to vary by more than 50% from one study to another, and these also appear to be dependent upon the method of determination[6,13].

Based on the aforementioned discussion, it is safe to conclude that the unified correlation developed herein, albeit limited to the five alkali metals, yields the values of the surface tension which are closer to the corresponding experimental values than those calculated using the predictive methods existing in the literature[3–6].

CONCLUDING REMARKS

In this work, new definitions of the reduced temperature and surface tension have been proposed which result in a unique functional dependence for the alkali metals. The variation of the reduced surface tension with the reduced temperature is found to be linear; the equation of the line has been obtained using the method of linear regression. The predicted values of the surface tension as well as those of the slopes are in excellent agreement with the corresponding actual values for temperatures ranging from the respective melting points all the way to the boiling points in each case.

NOMENCLATURE

A constant in Eq. (5), (−)
B constant in Eq. (5), (−)
T absolute temperature, (K)
T^* reduced temperature, (−)
T_b boiling point, (K)
T_c critical temperature, (K)
T_m melting temperature, (K)
σ surface tension, ($N\,m^{-1}$)
σ^* reduced surface tension, (−)
σ_b surface tension at boiling point, (Nm^{-1})
σ_m surface tension at melting point, (Nm^{-1})

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