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Note

Correlation of Surface Tension with Bulk Properties for Molten Alkali Halides

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The surface tension of alkali halide melts has been correlated with the bulk modulus and with the internal pressure. These are similar to those found earlier for liquid metals. The relationships, along with the volume expansion coefficients, can be used to calculate the temperature coefficient of surface tension.

KEY WORDS: alkali halides; bulk modulus; high temperature; internal pressure; surface tension.

1. INTRODUCTION

In the past few years, considerable evidence has been accumulated for relationships between bulk properties and the surface tension of liquids. For nonmetallic liquids, the surface tension has been shown to be directly proportional to the internal pressure [1] and to the function (density/compressibility)$^{1/2}$ [2], as well as to a function of the dielectric constant [3]. For liquid metals, following Skapski [4], Allen [5] has shown that the surface energy increases with the heat of vaporization. The plasma frequency has been correlated with liquid-metal surface tensions [6] and has been used to calculate the surface tension of binary alloys [7]. The surface tension of binary alloys, as well as liquid metals, has been related to the bulk modulus [8]. The temperature coefficients of surface tension for liquid metals have been calculated using the bulk modulus, internal pressure, and volume expansion [9].

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The purpose of the present communication is to show that the surface tension, γ, of molten alkali halides has the same relationship to the bulk modulus, β, as that for the liquid metals, i.e., $\gamma \sim \beta^{2/3}$. It was suggested earlier [8] that the surface tension was proportional to the surface elasticity, i.e., with $\beta^{2/3}$ dependence, which is the two-dimensional analogue to the three-dimensional bulk modulus. For liquid metals the internal pressure, P_i, was related to the surface tension $\gamma \sim P_i$, whereas for the molten alkali halides it appeared as $\gamma \sim P_i^{2/3}$. The relationships have been used to calculate the temperature coefficients of surface tension.

2. RESULTS

Figure 1 shows the correlation of surface tension with the bulk modulus and with the internal pressure for alkali halides. The values are tabulated in Table I. The values for β were taken from Kittel [10] except for the cesium salts, which were calculated from compressibility data [11]. All other parameters were taken from Ref. 12 except for the heats of vaporization at the melting point, ΔH_v, which were obtained from Janz

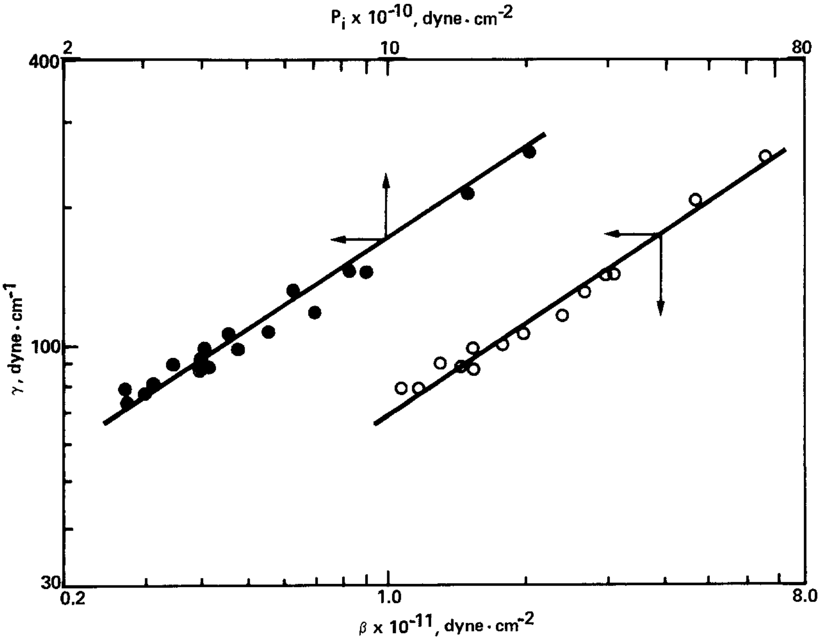

Fig. 1. Correlation of surface tension, γ, with bulk modulus, β, and with internal pressure, P_i, for alkali halides.

Table I. List of Properties Used for Eqs. (1) and (2)

Salt	γ^a (dyne·cm^{-1})	$\beta \times 10^{-11}$ (dyne·cm^{-2})	$P_i \times 10^{-10}$ (dyne·cm^{-2})	$\gamma_{calc.}/\gamma_{obs.}$ Eq. (1)	$\gamma_{calc.}/\gamma_{obs.}$ Eq. (2)
LiF	252	6.71	20.5	0.97	1.04
LiCl	138	2.98	9.02	1.02	1.11
NaF	201	4.65	15.2	0.95	1.08
NaCl	114	2.40	7.02	1.07	1.14
NaBr	106	1.99	5.55	1.02	1.05
NaI	88	1.51	4.0	1.02	1.02
KF	141	3.05	8.37	1.02	1.04
KCl	98	1.74	4.88	1.01	1.04
KBr	89	1.48	4.06	1.0	1.02
KI	79	1.17	3.15	0.96	0.96
RbF	130	2.62	6.34	1.0	0.94
RbCl	99	1.56	4.04	0.93	0.91
RbBr	91	1.30	3.47	0.89	0.89
RbI	81	1.06	2.72	0.88	0.85
CsF	107	—[b]	4.55		0.91
CsCl	91	—[b]	4.04		0.99
CsBr	83	—[b]	3.35		0.96
CsI	75	—[b]	2.79		0.94

[a] Surface tension at the melting point.

[b] Salts for which no information was found for the bulk modulus.

[13]. As before [8], the internal pressure was approximated as $P_i \approx \Delta H_v / V_m$, where V_m is the molar volume.

The fitted functions to the data shown in Fig. 1 are

$$\gamma = 3.17 \times 10^{-6} \beta^{2/3} \tag{1}$$

$$\gamma = 7.65 \times 10^{-6} P_i^{2/3} \tag{2}$$

where γ is in dyne·cm^{-1}, β is in dyne·cm^{-2}, and P_i is in dyne·cm^{-2}. The results obtained for calculated values of γ for both equations are compared and listed in Table I. The results are quite good.

Since $P_i = -T\alpha\beta$, where T is the temperature in K and α is the coefficient of thermal expansion in K^{-1}, differentiation of Eq. (2) with respect to T yields

$$7.10 \times 10^{7}\, \gamma^{1/2}\, d\gamma/dT = -[T\alpha(d\beta/dT) + T\beta(d\alpha/dT) + \alpha\beta] \tag{3}$$

Differentiating Eq. (1) with respect to temperature, one obtains $d\beta/dT$, which after substitution, along with Eq. (1) itself, into Eq. (3), yields

$$(1+3.75T\alpha)\,d\gamma/dT = -2.49\gamma[T(d\alpha/dT)+\alpha] \tag{4}$$

Equation (4) was used to calculate the temperature coefficients of surface tensions listed in Table II for those compounds for which linear thermal expansion coefficients as a function of temperature were available [11]. The linear expansion values were multiplied by 3 to obtain the volume expansion and were extrapolated to the melting point, with the slope of the line being $d\alpha/dT$. The results are quite good and generally better than those calculated for liquid metals. This is to be expected considering the difficulties associated with obtaining various experimental parameters for liquid metals.

The present results along with those for liquid metals give validity to surface tension correlations with bulk modulus and internal pressure. The correlations, through the thermodynamic basis for internal pressure, lead to reasonably good calculated values for the temperature coefficients of surface tension. The results of such calculations are, of course, dependent on the accuracy of the experimental parameters used.

Table II. Comparison of Calculated and Observed Temperature Coefficients of Surface Tension[a]

	$-d\gamma/dT$ (dyne · cm^{-1} · K^{-1})		
Salt	Obs.	Calc.	Calc./obs.
LiF	0.110	0.146	1.33
LiCl	0.070	0.071	1.01
NaF	0.108	0.071	0.66
NaCl	0.069	0.072	1.04
NaBr	0.068	0.045	0.66
NaI	0.050	0.039	0.78
KCl	0.071	0.042	0.59
KBr	0.071	0.056	0.79
KI	0.066	0.049	0.74
CsCl	0.076	0.037	0.49
CsBr	0.064	0.040	0.53
CSI	0.060	0.033	0.55

[a] Salts for which no information was found on thermal expansions are not listed.

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