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The cohesive energy density and the isothermal compressibility: Their relationships with the surface tension

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ABSTRACT

Models for predicting the cohesive energy density (*CeD*), the isothermal compressibility (k_T), the compressibility and surface tension product ($k_T.\gamma$), the ratio of surface tension to cohesive energy density (γ/CeD) and the isothermal compressibility and cohesive energy density product ($k_T.CeD$) are described. The temperature T at which the numerical constants are valid is the melting temperature. The studies are being restricted to alkali halides. The calculated ($k_T.\gamma$) values (21.3–40.9 pm), pertained to the sizes of voids between the ions, are of a smaller range than in the earlier treatments and agree very well with the experimental published data (21.9–47.6 pm). The determined (γ/CeD) values (4.3–8.2 pm), attributed to the contraction of the internuclear distance of the top-layer atoms in the surface, are comparable with the experimental data (3.9–11 pm). It is found that the ratio of the internuclear distance at the surface to that of the bulk is 97–98%.

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1. Introduction

A lot of attention has been paid to the scientific interest of the products of the isothermal compressibilities of liquids and their surface tensions [1–6]. However, there had been many limitations in these investigations because they either provide a single approximate value of the products ($k_T.\gamma$) for all liquids, or the parameters are not well defined or the calculated values are twice as large as the experimental data. The surface tension is inversely proportional to the isothermal compressibility, and their product is equal to 0.32 ± 0.15 Å for many liquids of dissimilar binding, including liquid metals, molten salts, organic liquids, aqueous solutions, and liquids of the common gases [5]. The product for the same liquids, at 298 K, has an average value 27 ± 3 pm and the distance ($k_T.\gamma$) is interpreted as the average elastic spacing between the stiff cores of the molecules, related to the multibody intermolecular potential function operating in 2π and 4π steradian space [7]. Others showed that the product of the compressibility and the surface tension of molten salts lies in the range 18.6–62.5 pm [8]. This length of a few tens of pm is too much smaller than the interionic distances in molten salts, and thus, it is not directly related to the sums of the sizes of the cations and anions and pertains rather to the sizes of the voids between the ions [8].

Surface tension (γ) is a type of force caused by unbalanced molecular attraction on liquid surface and it has effects in all dimensions. The direction of surface tension is tangent with the liquid surface, and is vertical to the division line of the two phases.

If the liquid surface is planar, the surface tension is upright on this plane whereas if it is a curved one, the surface tension is on a tangent plane [9]. Cohesive energy density (*CeD*) is a physical quantity used to characterize the strength of the interactive force among molecules of a substance [10]. A number of empirical equations have been reported for the relationship between the surface tension and the cohesive energy density such as proposed by Hildebrand and Scott [11,12], given as follows:

$$CeD = 16.8\left(\frac{\gamma}{V^{1/3}}\right)^{0.86} \quad (1)$$

where V is the molar volume of the substance. This equation is only suitable for non-associated small molecular systems.

This research paper reports models for calculating *CeD*, k_T, $k_T.\gamma$, (γ/CeD) and $kT.CeD$ of alkali halides, by correlating them with the internuclear distance (D). The results are compared with the existing data. The temperature T at which the numerical constants are valid is the melting temperature.

2. Theory and discussion

2.1. Isothermal compressibility and surface tension product

A semi-empirical formula is developed for predicting the compressibility and surface tension products ($k_T.\gamma$) for alkali halides. Theoretically, it is known that the $k_T.\gamma$ product yields a

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length (L) that represents the sizes of the voids between the ions [8], according to the following equation:

$$k_{T\cdot}\gamma = L \tag{2}$$

The L values that can be obtained from Eq. (2) are very high as compared to the experimental data (Table 1). Egelstaff and Widom [4] arrived at the expression:

$$k_{T\cdot}\gamma = 0.07L \tag{3}$$

Eq. (3) leads to values that are not consistent with the reported experimental data.

The applications of the scaled particle theory of Mayer and the simplified corresponding states correlation of Harada et al. [6] lead to calculated values twice as large as the experimental ones. The scientific significance and the new condensed-matter physics become clear by modifying Eq. (2). This is achieved by relating the product with the internuclear distance of the bulk (D^b) as shown by Eq. (4):

$$k_{T\cdot}\gamma = xD^b \tag{4}$$

where x (equal to 0.1058) is a semi-empirical fitting parameter. As seen in Table 1, Eq. (4) yields $k_T.\gamma$ values (21.3–40.9 pm) that are very much closer to experimental data (21.9–47.6 pm) than that reported by Marcus (18.6–62.5 pm) [8]. Therefore, it is a significant advancement in the subject of the compressibility–surface-tension product over what is already in the literature because a smaller range of this product than in the earlier treatments is obtained. However, it had already been observed [4] that the variation of that product for alkali halides is exceptionally narrow. The original and still the only interest in that product is in the very wide range of liquids to which it applies as compared with the (relatively) narrow range in its values. In this situation, it seems fair to say that the compressibility and surface tension product of alkali halides is equal to the internuclear distance multiplied by 0.1058. The products ($k_T.\gamma$) are, then, shown to depend solely on independent values of the internuclear distance of the bulk.

2.2. Ratio of surface tension to cohesive energy density

An important aspect of this work is, also, to evaluate the contraction of internuclear distance of the top-layer atoms in the surface of alkali halides. The surface tension (γ) is a fundamental thermodynamic quantity of liquids reflecting intermolecular interaction. The cohesive energy density (CeD) is a direct measure of the interaction energy between molecules. For many liquids, an empirical correlation between cohesive energy density and surface tension is long since known [13–15]. Both quantities are temperature-dependent parameters and are relative, and therefore, are specific thermodynamic values. The surface tension of alkali halides is proportional to their cohesive energy density because the packing of the fluid particles is more tight as the CeD becomes larger. The energy required to increase the surface is linearly proportional to the forces of attraction between the particles of a fluid. The internuclear distance at the surface is less than that in the bulk, and thus, the surface is slightly compressed relative to the bulk [4].

Although in the literature [16], the surface tension and the cohesive energy density were correlated for alkali halides [16] and for other materials [17–20], the relation between both quantities can be given as described in Eq. (5):

$$\left(\frac{\gamma}{CeD}\right) = C^n \tag{5}$$

where γ is the surface tension (mJ m^{-2}), CeD is the cohesive energy density (GPa or 10^9 J m^{-3}) and C^n is the contraction of the internuclear distance at the surface (pm). The γ and CeD data were taken from the literature (Table 1) [8,16,21]. The reported C^n values

Table 1
Calculated and reported contraction (C^n) of the top-layer internuclear distances at the surface, isothermal compressibility and surface tension product ($k_T.\gamma$), isothermal compressibility (k_T), cohesive energy density (CeD) and their product ($k_T.CeD$) of alkali halides, and the parameters needed for calculations.

Salt	T_m (K)	γ (Rep.) (mJ m^{-2})	k_T (GPa^{-1}) (Cal.)	k_T (GPa^{-1}) (Exp.)	CeD (Cal.) (GPa)	CeD (Rep.) (GPa)	$k_T.CeD$ (cal.)	$k_T.CeD$ (Rep.)	C^n (Exp.) (Eq. 5) (pm)	C^n (Cal.) (Eq. 11) (pm)	D^b (pm)	$k_T.\gamma$ (Cal.) (pm)	$k_T.\gamma$ (Exp.Rep) (pm)	$k_T.\gamma$ (Theor. Rep.) (pm)
LiF	1118	252	0.094	0.093	54.3	64.6	5.1	6.0	3.9	4.3	201	21.3	21.9	18.6
LiCl	878	138	0.230	0.216	22.4	28.4	5.2	6.1	4.9	5.3	249	26.3	28.3	24.7
LiBr	825	123	0.291	0.235	17.7	20.9	5.2	4.9	5.9	5.6	264	27.9	28.9	28.5
LiI	742	95	0.422	0.312	12.3	15.5	5.2	4.8	6.1	6.1	288	30.5	28.4	33.8
NaF	1266	187	0.127	0.133	40.5	39.4	5.1	5.2	4.7	4.9	231	24.4	24.7	21.7
NaCl	1074	106	0.264	0.343	19.5	17.7	5.1	6.1	6.0	5.9	279	29.5	36.4	31.2
NaBr	1020	93	0.325	0.361	15.8	14.6	5.1	5.3	6.4	6.3	294	31.1	33.6	34.9
NaI	934	80	0.449	0.436	11.4	10.8	5.1	4.7	7.4	6.8	318	33.6	34.9	42.2
KF	1131	132	0.216	0.186	23.7	22.9	5.1	4.3	5.8	5.7	266	28.1	26.6	27.3
KCl	1043	91	0.387	0.442	13.3	12.2	5.1	5.4	7.5	6.7	314	33.2	40.0	38.9
KBr	1007	82	0.461	0.465	11.1	10.2	5.1	4.7	8.0	7.0	329	34.8	38.1	43.8
KI	954	81	0.601	0.572	8.5	7.86	5.1	4.5	10.3	7.5	353	37.3	40.6	53.2
RbF	1068	125	0.270	0.176	19.0	18.6	5.1	3.3	6.7	6.0	281	29.7	22.4	30.4
RbCl	991	87	0.469	0.429	11.0	11.0	5.2	4.7	7.9	7.0	329	34.8	39.0	41.9
RbBr	966	84	0.550	0.499	9.3	9.3	5.1	4.6	9.0	7.3	344	36.4	41.9	47
RbI	920	71	0.706	0.607	7.3	7.4	5.2	4.5	9.6	7.8	368	38.9	43.1	47.9
CsF	955	104	0.369	0.228	13.9	15.6	5.1	3.6	6.7	6.4	300	31.7	24.5	33.6
CsCl	918	85	0.600	0.461	8.6	9.49	5.2	4.4	9.0	7.4	0.348	36.8	39.1	46.0
CsBr	909	77	0.687	0.584	7.5	8.01	5.2	4.7	9.6	7.7	363	38.4	45.0	52.1
CsI	894	69	0.845	0.690	6.1	6.3	5.2	4.3	11.0	8.2	387	40.9	47.6	62.5

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