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Fluid Phase Equilibria

Correlations of the surface tension and some thermodynamic and transport properties of the alkali metal halides at their melting temperatures based on their corresponding molar volumes

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ABSTRACT

Approximate expressions are proposed to determine the surface tension (γ), isothermal compressibility (k_T), cohesive energy density (CeD), surface tension and compressibility product ($k_T\gamma$), viscosity (η), self-diffusion coefficients (DC_{M+} and DC_{X-}) and cation–anion internuclear distance (D) of molten alkali halides, at melting temperatures (T). The validity of these expressions is tested for all the molten alkali halides, and the expressions hold well in most cases.

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1. Introduction

In view of numerous applications and importance in science and industry of molten alkali halides, an attempt is made to find a new way for correlating thermodynamic, thermophysical and transport properties of molten alkali halides, at the melting temperature. This paper demonstrates significant advances in the understanding of the physical properties of molten alkali halides. Alkali halides can be regarded as model ionic systems, and their various properties depending on molar volume and temperature are considered.

Molten alkali halides have industrially important characteristics, in addition to a scientifically interesting behavior, which justify the need for accurate thermophysical property data and the development of theoretical models for these systems. The viscosity and surface tension of high temperature melts, in general, are the most needed for industry purposes and unfortunately still the most poorly established properties. Although, considerable effort has been devoted in the past to the experimental measurement of these properties at high temperatures, the existent data is still very limited due to experimental difficulties related with some of the characteristics of these systems (e.g. strong chemical activity and high melting points). Due to these experimental measurements, in addition to the great number of systems of interest existent, it

becomes important to develop models capable of correlating these properties given a minimum amount of information as input.

Reiss et al. have obtained a precise equation of the state for the rigid-sphere fluid by computing the reversible work of creating a spherical cavity in this fluid [1–3]. Later, this approach has been extended to the surface tension [4,5] and to the isothermal compressibility [2,3] of molten alkali halides with the relationships shown in Eqs. (1) and (3), respectively:

$$\gamma = \left(\frac{DRT(2 + y)}{4V(1 - y)^2} \right) \tag{1}$$

$$y = \left(\frac{\pi D^3 N}{6V} \right) \tag{2}$$

$$k_T = \left(\frac{V(1 - y)^4}{RT(1 + 2y)^2} \right) \tag{3}$$

where γ is the surface tension ($\mathrm{J\,m^{-2}}$), V is the molar volume at the melting point ($\mathrm{m^3\,mol^{-1}}$), T is the melting temperature (K), R the universal gas constant ($8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$), N is Avogadro number ($6.02.10^{23}$ atoms/mol), k_T is the isothermal compressibility (Pa^{-1}) and D is the rigid-sphere diameter of the molecules comprising the pure liquid (m).

Mayer [4] combined Eqs. (1) and (3), and he obtained the surface tension and compressibility product ($k_T\gamma$) in the following form:

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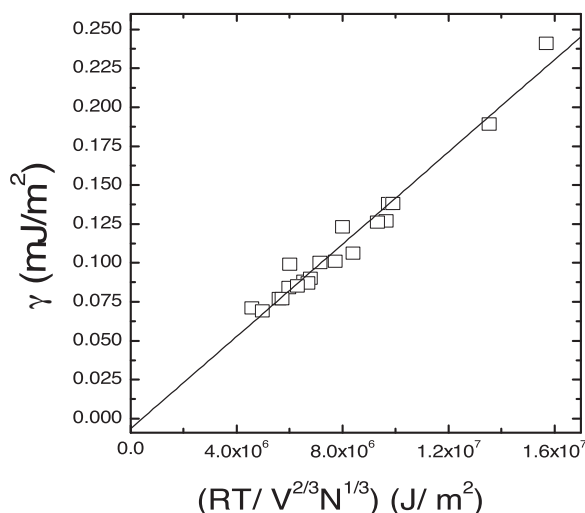 E-mail address: fathiaqra2009@hotmail.com (F. Aqra).

Fig. 1. Reported surface tension Ref. [10] versus $\left(RT/V^{2/3}N^{1/3}\right)$ of molten alkali halides.

$$k_T \gamma = \left(\frac{D(2 + 3y + y^2)}{4(1 + 2y)^2}\right) \quad (4)$$

At present, using molten salt as rigid sphere fluid is considered as outdated view, and this approach is especially inapplicable for the transport properties. This is obvious to anyone who examines the ABC-knowledge in molten salt physic and chemistry [6–8].

This article is a theoretical interesting and pretentious in that it claims to correlate the surface and bulk properties of molten alkali halides and is limited to their melting points, where excellent data already exist (except for some of the self-diffusion coefficients). On the other hand, it presents a number of useful and simple correlations with two readily available items for these salts: their melting points and molar volumes at these temperatures. Also, it describes properties of molten alkali halides using modeling. Eqs. (1),(3) and (4) are modified to give better results in such a way that new semi-empirical relations are developed and utilized to correlating various properties of molten alkali halides at the melting temperature. The calculated results are strictly compared with the reported data. The calculated values for all of the molten alkali halides are close to the experimental values. The results are of wide interest and likely to have a significant impact on the research community.

2. Theory and discussion

2.1. Surface tension

In the present study, Eq. (1) can be written in such a way as to provide a simple relationship for computing the surface tension of molten alkali halides. This expression, for the surface tension, can be described as shown in Eq. (5):

$$\gamma = 1.25\left(\frac{RT}{V^{2/3}N^{1/3}}\right) \quad (5)$$

where γ is surface tension ($J\,m^{-2}$) and 1.25 is a semi-empirical fitting parameter. A similar equation is previously published by Kaptay [9]. Fig. 1 is a plot of experimental surface tension data of molten alkali halides [10,11] with the term in Eq. (5). As seen, a linear relationship is obtained, thus, suggesting the validity of the expression. However, Eq. (5) has been checked against all the molten alkali halides, and it gave values that are in excellent agreement with the experimental data [10,11] (Table 1).

2.2. Isothermal compressibility

In a similar way, Eq. (3) is simplified, here, and it is rewritten as follows:

$$k_T = 0.0828\left(\frac{V}{RT}\right) \quad (6)$$

where k_T is the isothermal compressibility (Pa^{-1}). Fig. 2 is obtained by plotting the experimental isothermal compressibility data [10,12,13] with the term in Eq. (6). Once again, a linear relation is observed. The calculated compressibility values from Eq. (6) are consistent with the existing data [10,12,13] of molten alkali halides (Table 1).

2.3. Cation–anion internuclear distance

Stillinger [3] has shown that, when Eq. (3) is applied to molten alkali halides, values of the calculated cation–anion internuclear distances (D) are the same order of magnitude as those found for the solid alkali halides from X-ray diffraction data. In this study, it was considered worthwhile to establish an expression for calculating the cation–anion internuclear distance in molten salts. This relation is given as follows:

$$D = 0.79\left(\frac{V}{N}\right)^{\frac{1}{3}} \quad (7)$$

where D is the cation–anion internuclear distance (m). A plot of the experimental interionic distances [14] of molten alkali halides with the term in Eq. (7) results in a very good linearity (Fig. 3). The calculated values are very close to the reported data [14] (Table 2). On the other hand, Eq. (7) gives similar results as reported by Yajima et al. [15], where $D = (V/2N)^{1/3}$ because Yajima's expression is practically the same as that of the author, its coefficient $\left(2^{1/3}\right) = 0.79$ as the author's.

2.4. Cohesive energy density

Now that, it is of interest to determine, in anology, the cohesive energy density of molten alkali halides (CeD, Pa). A relatively simple and convenient relationship is developed as described in Eq. (8):
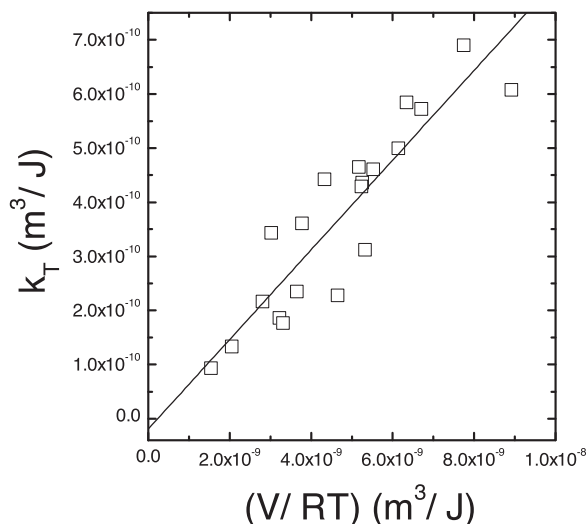

Fig. 2. Reported isothermal compressibility Ref. [10] versus (V/RT) of molten alkali halides.