

# Calculation of transport properties of molten salts using a double hard core model

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Received 11 April 1974

A method for the calculation of viscosity and electrical conductivity of molten alkali halides on the basis of the double hard core model proposed by Vasu was modified. Using the experimental data for cation— anion distance in the melt (or estimating this distance from the gas phase) and introducing a semi-empirical factor  $F$  allows one to obtain very good agreement between the calculated and experimental data both for the viscosity and for the electrical conductivity. It has been found that the semi-empirical factor  $F$  characterizing the geometrical arrangement of particles in the melt has a decreasing tendency in the series  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  except rubidium and cesium fluorides.

*Reiss, Frisch, Helfand, and Lebowitz* [1, 2] estimated the reversible work needed for creation of a spheric cavity in liquids composed of rigid spheres and derived the equation of state for these liquids

$$\frac{pV}{RT} = \frac{1 + Y + Y^2}{(1 - Y)^3}, \quad (1)$$

where  $p$  is the pressure,  $V$  is the molar volume and

$$Y = \frac{\pi a^3 N}{6V}, \quad (2)$$

where  $a$  is the diameter of the rigid spheres and  $N$  is the Avogadro number.

*Wertheim* [3] and *Thiele* [4] showed that the equation of state as derived by *Reiss et al.* [1, 2] is identical with the equation derived by *Percus and Yevick* [5] by an exact solution of the integral equation for the radial distribution function. *Lebowitz, Helfand, and Praestgaard* [6] generalized later the validity of this theory for the mixture of simple liquids. The same equation was derived by *Stillinger* [7] who showed that eqn (1) can be applied also to fused salts if we replace the fused salt by a rigid sphere fluid in which the particle diameter  $a$  equals the sum of the cation and anion radii.

Recently some thermodynamic properties of fused salts (entropy, heat capacity, entropy of fusion, compressibility, surface tension) have been calculated on the basis of this theory [8–11]. The agreement between calculated and experimental data is reported as good, and in some cases as very good. However, this model fails in the calculation of transport properties.

The results of the quoted works [1–7] were used by *Vasu* for the calculation of a contact correlation function in molten salts [12] on the base of double hard core model which

describes better the real situation in molten salts. Then the correlation function based on the double hard core model was applied in the calculation of viscosity [12] and electrical conductivity [13] of molten alkali halides. In this model Vasu takes into account coulombic interactions among particles in the melt and replaces them by double hard core interactions. It respects the fact that the ions of the same sign cannot come closer than to a certain distance which in the first approximation equals the minimum distance in the crystal lattice of NaCl type, *i.e.*  $a\sqrt{2}$  where  $a$  is the cation-anion distance. In the melt the distance can be even lower because the regular arrangement of particles in the lattice disappears after melting and the particles can be deformed and compressed. Further, it is known from the radial distribution functions that the coordination number decreases after melting from 6 to 3.5–5.6 [14]. Therefore in the melt of alkali halides one can assume that the minimum distance between the ions of the same sign can be expressed as  $aF$  where the value of the factor  $F$  will be lower than  $\sqrt{2}$ .

For the contact correlation function  $g(a)$  of oppositely charged ions which is important in the calculation of the transport phenomena it holds [12]

$$g(a) = \left(1 - \frac{Y}{2} + \frac{Y^2}{4}\right) (1 - Y)^{-3}, \quad (3)$$

where

$$Y = \frac{\pi a^3 N}{6V} (F^3 + 1). \quad (4)$$

In [12] the value of the geometrical factor  $F = \sqrt{2}$  was used.

Using Thorne's equation [15] for the viscosity of rigid spheres and eqns (3) and (4) Vasu derived for the viscosity of molten alkali halides the equation

$$\eta = \frac{0.419 Y^2 g(a)}{a^2} \left(\frac{m_1 m_2 kT}{m_1 + m_2}\right)^{1/2} \left\{1 + \frac{0.993}{Y g(a)} + \left[1 + 0.375 \frac{m_1 m_2}{(m_1 + m_2)^2}\right] \frac{0.475}{[Y g(a)]^2}\right\}, \quad (5)$$

where  $m_1$  and  $m_2$  are the masses of particles,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

On the base of kinetic theory of liquids Vasu derived also the following equation for electrical conductivity of molten salts [13]

$$\kappa = 3 e^2 \left[4 g(a) a^2 \sqrt{\frac{2\pi kT M_1 M_2}{M_1 + M_2}}\right]^{-1}, \quad (6)$$

where  $\kappa$  is the specific electrical conductivity,  $e$  is the charge of electron,  $M_1$  and  $M_2$  are the atomic weights of particles and the other symbols have the same meaning as mentioned above.

## Results and discussion

The calculation of the electrical conductivity and viscosity of molten alkali halides was carried out according to eqns (5) and (6) at the temperature  $T = 1.05 T^f$  (where  $T^f$  is the temperature of fusion). The influence of melting on the value of the geometrical factor  $F$  was taken into account. As it follows from eqn (4) the value of  $Y$  and thus also of the correlation function  $g(a)$  depends very much on the value of the product

$\alpha^3(F^3 + 1)$ , *i.e.* on the value of the cation–anion distance and on the factor  $F$ . In this work the experimental data for cation–anion distance as they were found from the diffraction studies of molten alkali halides [14] were used. Because these data are known only for 13 alkali halides, the rest of the data was estimated from the gas phase as it was recommended in paper [10]. The calculation of the viscosity and electrical conductivity was carried out for different values of the factor  $F$  which was changed with the step 0.01. As it follows from Table 1, one value of the factor  $F$  is suitable for the calculation of both the viscosity and the conductivity. The values of the molar volume are from [16]. The experimental data for viscosity and electrical conductivity are from the same work. The agreement between the calculated and experimental results is good and in some cases even excellent.

In the case of CsF the value of the factor  $F$  was determined only from the comparison between calculated and experimental electrical conductivity. The difference between these two values results only from that the factor  $F$  was determined with the accuracy of 0.01. The value of viscosity of CsF was predicted to be 2.08 cP. In the case of RbF neither viscosity nor electrical conductivity is known. The value of the factor  $F$  was assumed to be the same as in the case of CsF. Then the predicted value of the electrical conductivity of molten RbF is  $2.04 S\text{ cm}^{-1}$  and its viscosity 2.99 cP. Assuming the value of the factor  $F = 1.43$  it results  $\eta_{\text{cal}} = 1.82\text{ cP}$  and  $\kappa_{\text{cal}} = 3.26 S\text{ cm}^{-1}$ .

Table 1

Calculated and experimental viscosity (cP) and electrical conductivity ( $S\text{ cm}^{-1}$ ) of molten alkali halogenides ( $T = 1.05 T^{\circ}$ )

MX	$T$ [K]	$\alpha$ [Å]	$F$	$\eta_{\text{exp}}$	$\eta_{\text{cal}}$	$\kappa_{\text{exp}}$	$\kappa_{\text{cal}}$
LiF	1174	1.95 <sup>b</sup>	1.46	2.05 <sup>d</sup>	2.33	8.80	10.03
LiCl	927	2.47 <sup>b</sup>	1.45	1.49	1.58	5.95	5.92
LiBr	864	2.68 <sup>b</sup>	1.42	1.55	1.41	4.92	4.84
LiI	758	2.85 <sup>b</sup>	1.47	2.19	1.68	3.96	3.41
NaF	1331	2.30 <sup>b</sup>	1.38	1.65 <sup>e</sup>	2.07	5.10	5.55
NaCl	1127	2.80 <sup>b</sup>	1.35	1.19	1.26	3.74	3.98
NaBr	1074	2.98 <sup>c</sup>	1.34	1.23	1.34	3.06	2.98
NaI	982	3.15 <sup>b</sup>	1.38	1.31	1.31	2.40	2.49
KF	1185	2.70 <sup>b</sup>	1.31	—	1.72	3.73	3.60
KCl	1095	3.10 <sup>b</sup>	1.33	1.02	1.21	2.29	2.77
KBr	1058	3.30 <sup>c</sup>	1.30	1.04	1.32	1.74	2.02
KI	1006	3.53 <sup>c</sup>	1.31	1.43	1.43	1.38	1.48
RbF	1100	2.73 <sup>c</sup>	1.44	—	2.04	—	2.99
RbCl	1037	3.30 <sup>b</sup>	1.29	1.19	1.51	1.62	1.84
RbBr	1001	3.42 <sup>c</sup>	1.29	1.33	1.58	1.20	1.47
RbI	959	3.66 <sup>c</sup>	1.29	1.27	1.56	0.94	1.15
CsF	1003	2.82 <sup>c</sup>	1.44	—	2.08	2.53	2.63
CsCl	964	3.53 <sup>b</sup>	1.24	1.17	1.44	1.25	1.49
CsBr	954	3.55 <sup>b</sup>	1.29	—	1.61	0.91	1.25
CsI	939	3.85 <sup>b</sup>	1.26	1.66	1.70	0.73	0.88

b) see [14]; c) see [10]; d) see [17]; e) see [18].

It was found that the value of the factor  $F$  decreases in the series  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and has the mean value 1.45, 1.36, 1.31, 1.29, and 1.26 which can be explained by the dependence of this factor on the size and polarizability of ions. For lithium salts the value of the factor  $F$  is greater than  $\sqrt{2}$ . It is not surprising because in this case the effect of anion-anion repulsion can be considered. Similarly the effect of cation-cation repulsion is to be taken into account in the case of  $\text{RbF}$  and  $\text{CsF}$  where the value of the factor  $F$  is greater than  $\sqrt{2}$  as well. Similar argument was given by Yosim and Owens for the explanation of differences in the case of the calculation of the absolute entropy of these melts [10].

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Translated by P. Fellner