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Surface tension and cohesive energy density of molten salts

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ABSTRACT

The surface tensions σ of a large number of molten salts are known as (decreasing) linear functions of the temperature. They may be compared at a so-called "corresponding temperature", of which $1.1T_m$ is a good choice (T_m/K is the melting temperature). It is shown that for highly ionic molten salts of the 1:1, 1:2, and 2:1 charge types σ is a linear function of the cohesive energy density, *ced*. Molten salts with pronounced partial covalent bonding have generally much smaller surface tension values than highly ionic ones having similar values of the *ced*. The correlation between σ and *ced* is rationalized and compared with correlations in the literature, but the latter pertain only to the alkali metal halides.

1. Introduction

The surface tensions σ of many molten salts have been compiled by Janz and coworkers [1,2] as functions of the temperature and the data have been supplemented subsequently in several other publications, e.g., [3,4]. The values diminish linearly with increasing temperatures and ought to be compared at a suitable "corresponding temperature" as suggested by Reiss et al. [5]. As such, a temperature $1.1T_m$, somewhat above the melting point T_m, has been suggested [5,6] and applied in several studies [7–10]. For alkali metal halides, excepting the lithium salts, the surface tension at that temperature was correlated with the cube of the melting point [5]. Other correlations of σ with some other properties of molten salts have also been proposed [11,12], but again for a limited set of salts.

In this paper it is shown that the surface tensions σ at $1.1T_m$ of a large number of highly ionic molten salts of different types (1:1, 1:2, 2:1) correlate well with the cohesive energy densities *ced* of the salts, as far as such data could be ascertained. The rationale of this correlation is then briefly discussed.

2. The data

The corresponding temperatures, $1.1T_m$, the surface tensions, σ, and the cohesive energy densities, *ced*, of some 80 molten salts are listed in Table 1. The melting points T_m of the salts are generally from the $t_m/^\circ C = T_m/K - 273$ listed in the Handbook of Chemistry and Physics [13]. Where not otherwise noted, the σ values are calculated from the linear coefficients of $\sigma = a - b(T/K)$ given in [1]. A few additional sources of surface tension data are indicated in Table 1.

The cohesive energies, *ce*, of molten salts have been reported in [10] for most of the 1:1 salts and in [14] for most of the 1:2 and 2:1 salts. They were calculated from Eq. (1):

$$ce = -U_L + (H_{298} - H_0) + (H_{1.1Tm} - H_{298}) - \nu R(1.1\,T_m) \quad (1)$$

which is shown schematically in Fig. 1. The lattice potential energies $-U_L$ were from the compilation by Jenkins and Roobottom in [13]. Their relatively small corrections pertain to the raising of the temperature from 0 K to 298.15 K as $(H_{298} - H_0)$ with data from [15], and from 298.15 K through the melting process to $1.1T_m$ as $(H_{1.1Tm} - H_{298})$ with data from [16], and correcting from the enthalpies to the energies by $\nu R(1.1T_m)$, where ν is the number of ions per unit formula of the salt. It was noted that the corrections $(H_{298} - H_0) + (H_{1.1Tm} - H_{298})$ in those cases where they were available in [15] and [16] approximated $2\nu R(1.1T_m)$. Therefore, in the cases where $(H_{298} - H_0)$ and $(H_{1.1Tm} - H_{298})$ were not available the total correction could be estimated as $\nu R(1.1T_m)$, being $\leq 2\%$ of $-U_L$. The cohesive energy densities, *ced*, are then obtained by division of the *ce* values by the molar volumes of the molten salts, $V(1.1T_m)$, obtained from [17].

In those cases where the $-U_L$ values were not available in [13], they were estimated according to Jenkins et al. [18] using the

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Table 1
The corresponding temperatures, $1.1T_m$, the surface tensions, σ, from [1] unless otherwise noted, and the cohesive energy densities, *ced*, from [10,14] unless otherwise noted, of molten salts.

Salt	$1.1T_m$ (K)	σ (mJ m^{-2})	*ced* (GPa)	Salt	$1.1T_m$ (K)	σ (mJ m^{-2})	*ced* (GPa)
LiF	1232	241	64.6	MgF_2	1690	223[i]	110.1
LiCl	971	131[b]	28.4	$MgCl_2$	1057	67[h]	42.9
LiBr	902	123[e]	20.9	CaF_2	1860	284[i]	82.7
LiI	816	91[e]	15.5	$CaCl_2$	1151	140[h]	42.5
$LiNO_3$	578	113	20.1	$CaBr_2$	1103	115[h]	26.1
$LiClO_3$	441	85[h]	16.0[j,k]	CaI_2	1163	83[h]	22.6
Li_2CO_3	1109	245	60.4	$Ca(NO_3)_2$	906	102[h]	33.5[j]
Li_2SO_4	1245	225	38.4	SrF_2	1925	268[i]	67.0
Li_2MoO_4	1076[a]	214[d]	32.4[j]	$SrCl_2$	1261	161[h]	35.8
Li_2WO_4	1117[a]	217[d]	32.2[j]	$SrBr_2$	1008	146[h]	29.7
NaOH	656	151[f]	36.2	SrI_2	867	143[h]	27.1
NaF	1395	189	39.4	$Sr(NO_3)_2$	966	128[h]	27.4[j]
NaCl	1181	106	17.7	BaF_2	1805	221[i]	53.7
NaBr	1122	93	14.6	$BaCl_2$	1359	156[h]	30.2
NaI	1026	80	10.8	$BaBr_2$	1265	144[h]	25.4
$NaNO_2$	599	118	19.8[j]	BaI_2	1114	130[h]	22.9
$NaNO_3$	638	116	15.3	$Ba(NO_3)_2$	955	134[h]	22.5[j]
$NaClO_3$	573	87[c]	14.0[j]	$ZnCl_2$	650	54[h]	46.6
$NaBF_4$	749	84[m]	11.4	$ZnBr_2$	734	50[h]	39.9
Na_2CO_3	1244	206	41.2	$CdCl_2$	925	84[h]	46.5
Na_2SO_4	1273	185	24.9	$CdBr_2$	924	64[h]	36.5
Na_2MoO_4	1058	189[d]	26.4[j]	$PbCl_2$	851	138[h]	29.6
Na_2WO_4	1064	193[d]	25.7[j]	MgF_2	1690	223[i]	110.1
Na_3AlF_6	1407	118	36.0	$MgCl_2$	1057	67[h]	42.9
KOH	696	151[e]	23.6	CaF_2	1860	284[i]	82.7
KF	1244	135	22.9	$CaCl_2$	1151	140[h]	42.5
KCl	1154	91	12.2	$CaBr_2$	1103	115[h]	26.1
KBr	1108	82	10.2	CaI_2	1163	83[h]	22.6
KI	1049	71	7.86	$Ca(NO_3)_2$	906	102[h]	26.4[j,l]
KSCN	495	95	10.7	SrF_2	1925	268[i]	67.0
KNO_2	761	103	14.1[j]	$SrCl_2$	1261	161[h]	35.8
KNO_3	668	106	11.1	$SrBr_2$	1008	146[h]	29.7
$KClO_3$	643[n]	80[h]	11.3[j]	SrI_2	867	143[h]	27.1
KBF_4	927	73[g]	8.2	$Sr(NO_3)_2$	966	128[h]	27.4[j,l]
K_2CO_3	1289	159	27.3	BaF_2	1805	221[i]	53.7
K_2SO_4	1476	143[e]	17.0	$BaCl_2$	1359	156[h]	30.2
K_2MoO_4	1311	142	20.5[j]	$BaBr_2$	1265	144[h]	25.4
K_2WO_4	1314	148	27.9[j]	BaI_2	1114	130[h]	22.9
$K_2Cr_2O_7$	738	139	13.3[j]	$Ba(NO_3)_2$	955	134[h]	22.5[j,l]
RbF	1217	118	18.6	$LaCl_3$	1260	105[q]	54.6
RbCl	1087	91	11.0	$PrCl_3$	1165	104[r]	56.9
RbBr	1051	84	9.30	$SmCl_3$	1051	93[r]	57.2
RbI	1012	75	7.40	$ErCl_3$	1154	80[r]	61.2
$RbNO_3$	641	105	10.1	$YbCl_3$	1263	81[r]	63.1
Rb_2SO_4	1456	125	14.5	$ZnCl_2$	650	54[h]	46.6
CsF	1074	100	15.6	$ZnBr_2$	734	50[h]	39.9
CsCl	1011	85	9.49	$CdCl_2$	925	84[h]	46.5
CsBr	1000	77	8.01	$CdBr_2$	924	64[h]	36.5
CsI	989	69	6.30	$HgCl_2$	605	56[h,o]	41.4[j]
$CsNO_3$	756	87	8.05	$HgBr_2$	565	58[h]	36.0[j]
Cs_2CO_3	1173	128[e]	20.1[j]	$SnCl_2$	572	110[h]	40.7
Cs_2SO_4	1406	112[e]	9.7	$PbCl_2$	851	138[h]	29.6
AgCl	801	176[h]	53.7	$GaCl_3$	386	24[h]	58.8[j]
AgBr	778	152[h]	29.2	$BiCl_3$	556	65[h]	57.4
$AgNO_3$	534	146	17.7	$BiBr_3$	540	69[h,p]	34.1
$TlNO_3$	531	90	12.3[j]				

[a] The melting points are from [28].
[b] [5].
[c] [29].
[d] [30].
[e] [4].
[f] [31].
[g] [32].
[h] [2].
[i] [33], estimated at T_m from the scaled particle theory.
[j] See the text for the evaluation of these *ced* values.
[k] [20].
[l] [23].
[m] [3].
[n] At $T_m + 2 = 643$ K.
[o] At $T_m + 20 = 570$ K.
[p] The temperature coefficient −0.872 given in [2] is obviously a misprint, leading to negative values of σ; −0.072 yields a reasonable value commensurate with that of $BiCl_3$.
[q] From [34], extrapolated to pure molten $LaCl_3$.
[r] [35].