# Chapter 4
# Network Forming Ionic Liquids

## 4.1 Binary Network Forming Salts

Some inorganic salts associate in the molten state to large aggregates forming a network of bonds. Such a molten salt on cooling form a glass rather than crystallize. The glass is characterized by infinitely large viscosity and a loss of configurational entropy [1]. Among inorganic salts the foremost examples are $BeF_2$, $ZnCl_2$, $B_2O_3$, $SiO_2$, and $GeO_2$, the physicochemical data of which are shown in Table 4.1.

There is some information in the literature regarding these molten salts beyond the data in Table 4.1. The structure of the network forming salts has been studied by means of the methods already discussed in Sect. 3.2 for highly ionic high-melting salts. A common feature is the existence in the $MX_2$ melts of a close-packed anion ($X = F^-$, $Cl^-$, $O^{2-}$) structure with the multivalent cations ($M = Be^{2+}$, $Zn^{2-}$, $Si^{4+}$, $Ge^{4+}$) occupying tetrahedral sites in this structure. Thus networks of $MX_4^{2\text{ or }4-}$ tetrahedra that share corners are the common structural feature of these salts. This information resulted from the application of a variety of methods to the molten $MX_2$ salts: x-ray diffraction [22–24], neutron diffraction [24–27], XAFS [28, 29], Raman spectroscopy [30, 31], and computer simulations [24, 32–36]. Most of these reports dealt with $ZnCl_2$ [22, 24–28, 30, 32, 35], some of them with $ZnBr_2$ (a less pronounced network former) [25, 29, 30], and only very few with $BeF_2$ [33], $SiO_2$ [31, 32, 36], and $GeO_2$ [34]. (Studies of the structures of mixtures involving these compounds, e.g. LiF + $BeF_2$ and various non-stoichiometric silicates, are much more prolific).

The structure of molten $B_2O_3$ differs, in that three-fold coordination of boron atoms with oxygen atoms prevails in it [37–40]. The structure, obtained by x-ray diffraction at 923 K [37, 39] and up to 1073 K by neutron diffraction [38], thus involves hexagonal boroxol rings and independent $BO_3$ triangles, the proportion of the latter increasing with the temperature. Raman and luminescence studies of molten $B_2O_3$ at higher temperatures (up to 1700 K) showed further fragmentation to bent triatomic $BO_2^-$ units [40].

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**Table 4.1** Properties of binary glass-forming molten salts

| Property/units | $BeF_2$ | $ZnCl_2$ | $B_2O_3$ | $SiO_2$ | $GeO_2$ |
|---|---|---|---|---|---|
| Molar mass, $M$/kg mol$^{-1}$ | 0.04701 | 0.13632 | 0.06962 | 0.06008 | 0.10464 |
| Melting point, $T_m$/K[a] | 825 | 591 | 723 | 1996 | 1389 |
| Normal boiling point, $T_b$/K[a] | 1442 | 1005 | 2316 | 3070[t] | |
| Glass transition temperature, $T_g$/K | 523[b] | 375[c] | 545[d] | 1261[d] | 786[d] |
| Molar enthalpy of melting, $\Delta_m H$/kJ mol$^{-1}$[a] | 8.4 | 10.3 | 22.2 | 9.6 | 16.8 |
| Molar heat capacity at 1.1$T_m$, $C_P$/J K$^{-1}$ mol$^{-1}$[a] | 87.9 | 100.8 | 127.6 | 85.8 | 80.1 |
| Surface tension at 1.1$T_m$, $\sigma$/mJ m$^{-2}$ | 200[e] | 54[f] | 67[q] | 319[h] | 271[h] |
| Density at 1.1$T_m$, $\rho$/g cm$^{-3}$ | 1.990[f] | 2.492[f] | 1.630[g] | 2.209[o] | 3.488[i] |
| Molar volume at 1.1$T_m$, $V$/cm$^3$ cm$^3$mol$^{-1}$ | 23.6[f] | 54.7[f] | 42.7[g] | 27.2[o] | 30.0[i] |
| Isobaric expansibility at 1.1$T_m$, $10^6\alpha_P$/K$^{-1}$ | 260[f] | 186[f] | 82.4[g] | 37[o] | 8.9[i] |
| Isothermal compressibility at 1.1$T_m$, $\kappa_T$/GPa$^{-1}$ | | 0.547[l] | 0.05[i] | 0.007[i] | 0.121[i] |
| Internal pressure 1.1$T_m\alpha_P/\kappa_T$, $P_{int}$/MPa | | 221 | 1311 | 10,550 | 112 |
| Viscosity coefficient, $A_\eta$ | 22.4[f] | 8.15[f] | 6.3[k] | 16.7[j] | 6.16[m] |
| Viscosity coefficient, $B_\eta$/kJ | 244.1[f] | 75.1[f] | 89.2[k] | 516.0[j] | 186.3[m] |
| Viscosity at 1.1$T_m$, $10^{-3}\eta$/Pa s | 20.62[f] | 0.315[f] | 1.67[k] | 96.7[j] | 44.4[m] |
| Equivalent conductivity coefficient, $A_\Lambda$ | 44.37[n] | 11.46[p] | | | |
| Equivalent conductivity coefficient, $B_\Lambda$/kJ | −197[n] | −0.92[p] | | | |
| Equivalent conductivity at 1.1$T_m$, $\Lambda$/S Scm$^2$ cm$^2$mol$^{-1}$ | 0.0002[n] | 9.67[p] | $9.2 \times 10^{-6}$[s] | $7.5 \times 10^{-4}$[r] | |

The viscosity entries pertain to $\ln(\eta/\text{Pa s}) = A_\eta \exp(B_\eta/RT)$ and the conductivity entries to $\ln(\Lambda/\text{S cm}^2\ \text{mol}^{-1}) = A_\Lambda \exp(-B_\Lambda/RT)$

[a][2], [b][3], [c][4], [d][5], [e][6] (assumed value), [f][7], [g][8], [h][9], [i][10], [j][11], [k][12], [l][13], [m][14] used ($T$/K – 199) instead of $T$/K in the denominator, [n][15], [o][16], [p][17], [q] [18], [r][19], with $\kappa$ read from a curve, [s][20], with $\kappa$ read from a curve, [t][21]

The glass transition temperature $T_g$ (the temperature at which on cooling a liquid the viscosity reaches the value of $10^{12}$ Pa s) recorded in Table 4.1 can be interpreted in several manners. These include the temperature at which, on super-cooling of the melt, the free volume $V_f$ vanishes or the heat capacity undergoes a deep decline, $\Delta C_P$, to below the crystal values. For glass forming substances the Arrhenius-type dependence of transport properties, $\ln(\eta/\text{Pa s}) = A_\eta \exp\left(B_\eta/RT\right)$ for the viscosity, may have to be changed to the Vogel- Fulcher-Tammann- (VFT) form:

$$\eta/\text{Pa s} = A_\eta{}' \exp\left(B_\eta{}'/R(T - T_0)\right) \tag{4.1}$$

where $T_0 < T_g$. At temperatures not far from the melting point the transport phenomena (viscosity, conductivity, self-diffusion of the ions) depend on the temperature according to the Arrhenius expression with the coefficients $A_\eta$ and $B_\eta$ for the viscosity (and corresponding ones for the conductivity) shown in Table 4.1. However, deviations may occur at higher temperatures and definitely do so for the super-cooled liquids. The apparent activation energy $B_\eta$ declines at higher temperatures in the cases of $B_2O_3$ and $SiO_2$ and appears to do so also in those of $BeF_2$ and $GeO_2$ [41], a behavior attributed to the breakdown of the network to smaller fragments. This finding was challenged in the case of $B_2O_3$ [12], where true Arrhenius-type behavior of the viscosity was found above 1073 K, and in the case of $BeF_2$ [42] where such behavior was found all the way up to 1250 K. On the other hand, the VFT expression was found to describe accurately the viscosity of $SiO_2$ and $GeO_2$ over at least 12 orders of magnitude [14], with $T_0 = 530$ K and 199 K respectively. The original data were re-examined here and the VFT expression holds very well for $ZnCl_2$ at $598 \leq T/\text{K} \leq 716$ [43] or $600 \leq T/\text{K} \leq 893$ [44] and for $ZnBr_2$ at $673 \leq T/\text{K} \leq 813$ [44] with the same $T_0 = 260$ K (The $T^{1/2}$factor used in [43] is unnecessary, because it varies only by 9 % over the $T$-range studied). The same VFT expression with $T_0 = 260$ K holds also for the viscosity, specific conductance, and self-diffusion coefficients of zinc and chloride ions in molten $ZnCl_2$, albeit for much fewer data [17].

## 4.2 Molten Borates and Silicates

Physicochemical data of borate and silicate melts having stoichiometric compositions are shown in Table 4.2. Although a large amount of information regarding mixtures of molten oxides or molten silicates and borates can be found in the literature, data regarding pure, stoichiometric single compounds is relatively scarce.

Some information beyond what is shown in Table 4.2 has been reported. The adiabatic compressibility, obtained from sound velocity and density data (Sect. 3.3.3) was reported [55] as $\kappa_S/\text{GPa}^{-1}$ at 1473 K for $Na_2SiO_3$ (0.588), $Na_2Si_2O_5$ (0.643), $K_2SiO_3$ (1.27), $K_2Si_2O_5$ (0.791), and at 1173 K for $LiBO_2$ (1.205) and $Li_2B_4O_7$ (1.29). The isothermal compressibility $\kappa_T/\text{GPa}^{-1}$ (the reciprocal of the bulk

**Table 4.2** The molar masses, $M$, melting points, $T_m$, molar enthalpies of melting, $\Delta_m H$, constant pressure molar heat capacities, $C_p$, (from [2]), and the molar volumes, $V$, isobaric expansivities, $\alpha_P$, and viscosities, $\eta$, at $1.1T_m$ of molten silicates and borates

| Salt, | $M$ | $T_m$ | $\Delta_m H$ | $C_p$ | $V$ | $10^3\alpha_P$ | $\eta$ |
|---|---|---|---|---|---|---|---|
|  | kg mol$^{-1}$ | K | kJ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | cm$^3$ mol$^{-1}$ | K$^{-1}$ | Pa s |
| $Li_2SiO_3$ | 0.08997 | 1474 | 28.0 | 167.4 | $21.8^{f}$ | $0.107^{f}$ |  |
| $Li_2Si_2O_5$, | 0.15005 | 1307 | 53.8 | 251 | $23.4^{v}$ |  |  |
| $LiBO_2$ | 0.04975 | 1117 | 33.9 | 144.6 | $26.5^{u}$ | $0.247^{u}$ |  |
| $Li_2B_4O_7$ | 0.16912 | 1190 | 120.5 | $470.6^{a}$ | $89.0^{i}$ | $0.218^{i}$ |  |
| $Na_2SiO_3$ | 0.12206 | 1362 | 51.8 | 177.3 | $27.2^{f}$ | $0.128^{f}$ | $132^{w}$ |
| $Na_2Si_2O_5$ | 0.18215 | 1147 | 35.6 | 261.2 | $79.4^{u}$ | $0.096^{u}$ |  |
| $NaBO_2$ | 0.06580 | 1239 | 36.2 | 146 | $35.5^{y}$ | $0.359^{y}$ |  |
| $Na_2B_4O_7$ | 0.20122 | 1016 | 81.2 | 444.9 | $99.8^{p}$ | $0.427^{p}$ | $7.0 \times 10^{-3\ n}$ |
| $K_2SiO_3$ | 0.15428 | $1249^{b}$ | $50.2^{z}$ | $167.4^{z}$ | $35.3^{f}$ | $0.160^{f}$ |  |
| $K_2Si_2O_5$ | 0.21436 | $1318^{c}$ | $35.2^{z}$ | $275.3^{z}$ | $95.9^{u}$ | $0.125^{u}$ |  |
| $K_2B_4O_7$ | 0.23344 | 1088 | 104.2 | $473.2^{a}$ | $125^{m}$ |  |  |
| $MgSiO_3$ | 0.10039 | 1850 | 75.3 | $146.4^{z}$ | $39.3^{h}$ | $0.07^{h}$ | $0.164^{k}$ |
| $Mg_2SiO_4$ | 0.14069 | 2171 | 71.1 | $205.0^{z}$ |  |  |  |
| $CaSiO_3$ | 0.11616 | 1813 | 56.1 | 151 | $44.7^{h}$ | $0.07^{h}$ | $0.120^{k}$ |
| $CaB_2O_4$ | 0.12570 | 1433 | 74.1 | 258 |  |  |  |
| $CaB_4O_7$ | 0.19532 | 1263 | 113.4 | 444.8 |  |  |  |
| $SrSiO_3$ | 0.16370 | $1851^{d}$ | $56^{e}$ |  |  |  | $0.139^{k}$ |
| $Sr_2SiO_4$ | 0.26732 | $2598^{e}$ |  |  |  |  |  |
| $SrB_4O_7$ | 0.24286 | $1267^{l}$ | $139.8^{l}$ |  |  |  |  |
| $BaSiO_3$ | 0.21341 | $1877^{d}$ | 139.8 |  |  |  | $0.117^{k}$ |
| $BaB_4O_7$ | 0.29257 | $1182^{l}$ |  |  |  |  |  |
| $MnSiO_3$ | 0.13102 | 1543 | 66.9 | 153.8 |  |  | $0.043^{k}$ |
| $Mn_2SiO_4$ | 0.20196 | 1613 | 94.6 | 230.1 |  |  | $180^{x}$ |
| $Fe_2SiO_4$ | 0.20377 | 1493 | 92 | 240.6 | $18.3^{x}$ | $7.0^{x}$ | $520^{x}$ |
| $ZnSiO_3$ | 0.14149 | $1710^{d}$ |  |  |  |  |  |
| $Zn_2SiO_4$ | 0.22290 | $1783^{d}$ |  |  |  |  |  |
| $CdSiO_3$ | 0.18849 | $1516^{d}$ |  |  |  |  |  |
| $Cd_2SiO_4$ | 0.31691 | $1516^{d}$ |  |  |  |  |  |
| $PbSiO_3$ | 0.28328 | 1037 | 26.0 | 130.1 |  |  |  |
| $Pb_2SiO_4$ | 0.50648 | 1016 | 51.0 | 189.1 |  |  |  |

[a] At 1.1 $T_m$, [b][45], [c][46], [d][47], [e][49], [f][48] (according to [53] $V = 69.0$ cm$^3$ mol$^{-1}$ at $1.1T_m$), [g][8], [h][50], [i][51], [j][11], [k][12], [l][52], [m][53], [n][54], [o][16], [p][18], [u][55], [v][56] at 1673 K, [w][57], [x][58] (at 1873 K for $Mn_2SiO_4$), [y][59], [z][71]

modulus) is 0.050 for $MgSiO_3$ at 1913 K and 0.040 for $CaSiO_3$ at 1836 K [50, 60]. The viscosity of $Na_2Si_2O_5$ follows the VFT expression (4.1) with $A_\eta' = 0.0611$, $B_\eta' = 31.5$ kJ mol$^{-1}$, and $T_0 = 454.5$ K [57]. The surface tension of calcium silicates, $\sigma$/mN m$^{-1}$, hardly varies between 1780 and 1870 K: it is 530 for $CaSiO_3$ and 450 for $CaSi_2O_5$ (read from a curve [61]). The thermal conductivity of $Na_2SiO_3$ follows the

Arrhenius expression $\ln\left(\lambda_{\mathrm{th}}/\mathrm{W\ m^{-1}K^{-1}}\right) = -14.5 + 20319/T$, i.e., with an activation energy $B_{\lambda} = 170$ kJ mol$^{-1}$ [62].

Molecular dynamics simulation of $Mg_2SiO_4$ [63] yielded values for the isothermal compressibility $\kappa_T = 0.025$ GPa$^{-1}$ at 2100 K, the density at 2110 K and at 2 GPa $\rho = 2.75$ g cm$^{-3}$ (read from a figure) and the molar volume $V = 51$ cm$^3$ mol$^{-1}$, and an average molar isochoric heat capacity $C_V = 200$ J K$^{-1}$ mol$^{-1}$. The self-diffusion coefficients for $Mg_2SiO_4$ at low pressures are $D/\mathrm{m^2\ s^{-1}} = 2.6 \times 10^{-7}$ $\exp\left(66.4\ \mathrm{kJ\ mol^{-1}}/RT\right)$ for Mg and $1.7 \times 10^{-7}$ $\exp(79.2\ \mathrm{kJ\ mol^{-1}}/RT)$ for Si, and the dynamic viscosity is $\eta/\mathrm{Pa\ s} = 4.5 \times 10^{-4}\exp\left(41.0\mathrm{kJ\ mol^{-1}}/RT\right)$.

The structures of only a few of the stoichiometric molten borates and silicates (among those listed in Table 4.2) has been determined. The molecular dynamics simulation of $Mg_2SiO_4$ [63]. at relatively low pressures showed that >75 % of the silicon atoms are tetrahedrally surrounded by oxygen atoms, the rest mainly in fivefold coordination defining distorted trigonal bipyramidal polyhedra. At low pressure, the average coordination number of the Mg atoms is ≈5.5. As the pressure increases the average coordination number increases (~7.5) near 100 GPa. Octahedrally coordinated Mg attains a maximum at about 20 GPa and decreases systematically as the pressure increases. X-ray absorption spectroscopy of liquid $Fe_2SiO_4$ at 1575 K and ambient pressure [64] showed ~11 % shortening of the Fe–O distance in the melt compared with the crystal at the melting point, and a similar increase in the volume, indicating a decrease of the average coordination number of the Fe from 6 in the crystal to 4 in the melt, i.e., both Fe(II) and Si(IV) are tetrahedrally coordinated. Neutron diffraction with isotope substitution (see Sect. 3.2) was applied to molten $Li_2B_4O_7$ [65] and to molten $CaSiO_3$ [66]. For the former the Li–O distance decreased somewhat and that of Li–B increased at 1073 K compared to the glassy state, signifying an increase in the non-bridging oxygen content in the lithium coordination in the melt. In the latter salt the melt comprises primarily six- and sevenfold Ca–O coordination. Short chains of edge-shared Ca-octahedra feature in the structure of molten $CaSiO_3$.

A molecular dynamics simulation [67] showed similarities between alkaline earth silicates and alkali metal fluoroberyllates of the stoichiometries $MSiO_3$ with $M'BF_3$ and $M_2SiO_4$ with $M'_2BeF_4$ at corresponding temperatures ~$1.1T_m$ when having cations of similar sizes ($Li^+$ and $Mg^{2+}$, $Na^+$ and $Ca^{2+}$, $K^+$ and $Ba^{2+}$). The structures contain monomer, dimer, chain, and sheet units and experimental determinations of properties of fluoroberyllates in the more readily accessible range 620–1070 K could replace those on silicates, pertinent to geological problems, at the higher range of 1700–3000 K.

Another topic that pertains to the molten borate and silicate salts and to oxide melts in general is their acid-base behavior, in which oxygen atoms take the place of the hydrogen ions commonly encountered in aqueous solutions. Flood and Förland [68] established the concept of 'oxoacidity' and introduced the quantity $\mathrm{pO} = -\log a_O$, the negative of the logarithm of the oxygen activity in the melt, analogous to the pH. Dron [69] applied this framework to molten silicates, starting with equilibria such as $MSiO_3 + MO \leftrightarrows M_2SiO_4$, involving free $O^{2-}$ ions and bridging and non-bridging oxygen atoms. Konakov [70] reviewed the application of the acid-base concept to oxide melts via the pO scale and discussed the use of the stabilized zirconia electrode ($ZrO_2$ stabilized by 5 % CaO or $Y_2O_3$) to its measurement. The electrochemical cells to be used consist of molten silica, $SiO_2$, as the standard, and the pO of other oxide melts is measured relative to this standard, assigned pO = 7. A secondary standard of $Na_2SiO_3$ was established, with pO = 5.88. Applications to binary alkali metal borate, silicate, and germanate systems were reviewed.

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