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The structure of molten zinc chloride and potassium chloride mixtures

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Abstract. The structures of molten mixtures of zinc chloride and potassium chloride have been investigated by pulsed neutron diffraction. Total structure factors have been determined for natural samples of the two pure salts and for mixtures across the composition range using the Liquids and Amorphous Materials Diffractometer at the Rutherford–Appleton Laboratory's ISIS source. The results show that the tetrahedral coordination of anions around zinc ions is present right across the composition range and species of a lower coordination number are not formed. Furthermore, the intermediate-range ordering found in pure zinc chloride is persistent in the mixtures right up to high potassium chloride concentrations. The results are consistent with a recent clustering model, proposed as an explanation for the origin of medium-range ordering in molten salts.

1. Introduction

The partial structure factors of the two pure molten salts ZnCl_2 and KCl have been measured by neutron diffraction using the isotopic substitution method by Biggin and Enderby (1981) and Derrien and Dupuy (1975). For ZnCl_2 , both x-ray diffraction (Triolo and Narten 1981) and EXAFS studies (Wong and Lytle 1980) have confirmed the results of Biggins and Enderby and show that the melt consists of a closely packed chloride structure in which Zn^{2+} ions reside in tetrahedrally coordinated sites. The anomalously low electrical conductivity of molten ZnCl_2 (Grantham and Yosim 1966), its high viscosity (Susic and Mentus 1975) and its glass-forming ability have led to the description of ZnCl_2 as a 'network melt', in which ZnCl_4^{2-} tetrahedral units are linked via corner sharing of chloride ions to form a network. Furthermore, a recent pulsed neutron diffraction study by Allen *et al* (1991) has revealed that the basic ZnCl_4 structural unit is extremely well defined, with little ionic exchange into and out of the first coordination shell.

An interesting feature of the diffraction studies of molten ZnCl_2 and other divalent cation halides has been the observation of a sharp diffraction peak at $Q \approx 1 \text{ \AA}^{-1}$, which has its origin in the cation–cation partial structure factor. This has been interpreted as indicating ordering between cations of an intermediate range, possibly arising from angular dependence of interionic forces (Wood and Howe 1988).

The addition of an alkali halide to molten ZnCl_2 makes possible the formation of isolated structural entities by providing additional halide ions and reducing the need for

corner sharing between the tetrahedra. Indeed, Raman scattering studies of molten mixtures of zinc halides with alkali halides by Ellis (1966) have shown that, when an alkali halide is added to molten ZnCl_2 , stretching modes associated with bridging chloride ions between tetrahedral units are reduced, while bands related to isolated ZnCl_n^{2-n} units emerge. This has led to the description of the alkali halide as a 'network breaker' which breaks the polymeric network of molten ZnCl_2 by providing extra chloride ions. Isolated ZnCl_n^{2-n} complexes can then form within a sea of alkali metal counter ions. If intermediate-range order has its origin in the angular dependence of interionic forces, then it might be expected to diminish with the formation of these isolated ZnCl_n^{2-n} complexes.

The paper reports the results of a pulsed neutron diffraction investigation of molten mixtures of ZnCl_2 with KCl. In order to follow the structural changes which occur upon mixing the two salts, measurements were made for a number of mixtures across the composition range. The samples were not isotropically enriched, but interpretation of the total structure factors and distribution functions has been aided by the availability of partial structure factors and distribution functions for the two pure salts.

2. Neutron diffraction from liquids

The quantity which can be determined from a single neutron diffraction experiment on a liquid containing three atomic species a, b and c with concentrations C_a , C_b and C_c is the total structure factor $F(Q)$, defined by

$$F(Q) = C_a^2 b_a^2 [S_{aa}(Q) - 1] + C_b^2 b_b^2 [S_{bb}(Q) - 1] + C_c^2 b_c^2 [S_{cc}(Q) - 1] \\ + 2C_a C_b b_a b_b [S_{ab}(Q) - 1] + 2C_a C_c b_a b_c [S_{ac}(Q) - 1] \\ + 2C_b C_c b_b b_c [S_{bc}(Q) - 1] + 1 \quad (1)$$

where b_a , b_b and b_c are the coherent scattering lengths of the three species and the $S_{\alpha\beta}$ are the six partial structure factors, defined according to the definition of Faber and Ziman (1965). The total structure factor is related by Fourier transformation to the total distribution function $G(r)$ by

$$G(r) = 1 + \frac{1}{2\rho_0\pi^2 r} \int_0^\infty QF(Q) \sin(Qr) dQ \quad (2)$$

where ρ_0 is the mean atomic number density. $G(r)$ is a linear combination of the pair distribution functions $g_{\alpha\beta}$ weighted by the coefficients of equation (1) so that

$$G(r) = 1 + C_a^2 b_a^2 [g_{aa}(r) - 1] + C_b^2 b_b^2 [g_{bb}(r) - 1] + C_c^2 b_c^2 [g_{cc}(r) - 1] \\ + 2C_a C_b b_a b_b [g_{ab}(r) - 1] + 2C_a C_c b_a b_c [g_{ac}(r) - 1] \\ + 2C_b C_c b_b b_c [g_{bc}(r) - 1]. \quad (3)$$

The scattering of thermal neutrons has been measured by the time-of-flight technique from samples of molten ZnCl_2 and KCl and from molten mixtures of these two salts with KCl concentrations of 33.3%, 50%, 66.7%, 81%, 90% and 95%. Descriptions of these

Table 1. Data analysis parameters and the coherent scattering contributions of the particles to the total $F(Q)$ for the mixtures studied or for the zinc chloride and potassium chloride mixtures. The figures in parentheses are the percentage contributions of each partial to $F(Q)$.

Concentration (% KCl)	Density (g cm ⁻³)	Coherent scattering coefficient (b)					
		Zn-Zn	K-K	Zn-K	Cl-Cl	Zn-Cl	K-Cl
Pure ZnCl ₂	2.52 at 330 °C 2.40 at 600 °C	0.0358 (5.2)			0.4078 (59.5)	0.2418 (35.3)	
33.3 ± 0.2	2.31 at 340 °C 2.25 at 450 °C	0.0202 (3.2)	0.0022 (0.3)	0.0132 (2.1)	0.3584 (57.9)	0.1700 (27.5)	0.0555 (9.0)
50.1 ± 0.3	2.16 at 340 °C 2.11 at 450 °C	0.0130 (2.2)	0.0055 (0.9)	0.0169 (2.9)	0.3303 (56.8)	0.1306 (22.5)	0.0853 (14.7)
66.6 ± 0.3	1.98 at 450 °C	0.0066 (1.2)	0.0113 (2.1)	0.0172 (3.2)	0.2992 (55.5)	0.0889 (16.5)	0.1161 (21.5)
81.0 ± 0.3	1.61 at 820 °C	0.0024 (0.5)	0.0188 (3.8)	0.0135 (2.7)	0.2710 (54.2)	0.0513 (10.3)	0.1429 (28.6)
90.0 ± 0.4	1.56 at 820 °C	0.0007 (0.2)	0.0253 (5.4)	0.0086 (1.8)	0.2518 (53.2)	0.0271 (5.7)	0.1596 (33.7)
94.9 ± 0.4	1.53 at 820 °C	0.0002 (0)	0.0295 (6.4)	0.0049 (1.1)	0.2409 (52.6)	0.0139 (3.0)	0.1685 (36.8)
Pure KCl	1.50 at 820 °C		0.0344 (7.8)		0.2294 (52.0)		0.1777 (40.2)
	σ_c (b)	σ_s (b)	σ_a (b) (at 1.798 Å)				
Zinc	4.054	4.133	1.11				
Potassium	1.73	1.98	2.1				
Chlorine	11.531	16.7	33.5				

The scattering cross-sections used were from Sears (1984).

samples and the parameters used for the data analysis are listed in table 1, where the percentage contribution to the total coherent scattering from each partial component is also shown.

3. Experimental details

Quantities of the two pure salts were dried separately by heating slowly under vacuum. ZnCl₂ was held at 100 °C at a pressure of 5×10^{-2} mbar for 5 d. KCl was heated to 200 °C over a period of about 4 d at a pressure of 5×10^{-6} Torr. For the mixtures, weighed quantities of the two dried salts were mixed in an evacuable glove box filled with dry argon before being sealed into fused quartz containers and melted for 24 h at temperatures in excess of the liquidus temperatures. According to the phase diagram (Perry *et al* 1983) these two salts mix readily across the composition range, with three eutectics at 27%, 50% and 71% KCl concentrations, and solid state compound formation at 33.3%, 60% and 66.7% concentrations. All the samples were loaded in a dry argon atmosphere into fused quartz tubes of internal diameter 8 mm and wall thickness of 1 mm, before being sealed at a pressure of 2/3 atm.

The neutron scattering spectra were measured by time-of-flight analysis on the Liquids and Amorphous Materials Diffractometer at the Rutherford-Appleton Laboratory's pulsed neutron source, ISIS. The measurements were made at a temperature just above the melting point of ZnCl_2 wherever that was possible. However, at the KCl-rich end of the phase diagram, the rising liquidus required that a higher temperature was used, and measurements were made at a temperature just above the melting point of KCl. In order to distinguish temperature from composition effects, measurements were also made at 450 °C for the 33.3% and 50% KCl mixtures and at 600 °C for pure ZnCl_2 . The samples were held at a constant temperature (± 1 °C) using a vanadium foil furnace designed and built by the Leicester group. As a check on the microscopic mixing of the two components, data for the mixtures was recorded after every 2 or 3 h. After normalization to the incident flux for each counting period no change in scattering with time was observed for any of the mixtures. In addition, the scattering from the positive- and negative-angle counter banks at each detector angle showed good agreement. Structure factors were obtained for each detector angle after correcting the scattering intensities for background and container scattering, absorption effects, and incoherent and multiple scattering in the manner described by Howells (1986). Normalization was achieved by reference to the scattering from a vanadium rod.

The data sets for the different detector angles were then combined, using a flux-weighting technique similar to that described by Wood *et al* (1988), over the Q -ranges for which there was good overlap agreement between the different detectors. This was typically over a wavelength range from 0.3 to 1.3 Å for the detectors at $\pm 10^\circ$, $\pm 20^\circ$, $\pm 35^\circ$, $\pm 58^\circ$ and $\pm 90^\circ$. The $\pm 5^\circ$ detectors lacked sufficient resolution to be useful and the $\pm 150^\circ$ detectors were included with a lower Q -limit of 13 Å⁻¹. For consistency, the same spectral ranges were used for all the samples and the resulting composite structure factors can be seen in figure 1. The long-wavelength limits of $F(Q)$ for the two pure salts were calculated from their isothermal compressibilities (Janz 1967). They were 0.37 for ZnCl_2 and 0.53 for KCl. The structure factors for these two salts were extrapolated at low Q to these limits prior to Fourier transformation. For the mixtures, however, the absence of any compressibility information meant that the long-wavelength limits of $F(Q)$ had to be estimated. However, the Fourier transform is insensitive to this region of Q -space; so uncertainty in the values of $F(0)$ is of little consequence for the real-space functions.

The structure factors have been Fourier transformed to produce the total radial distribution functions shown in figure 2. For those mixtures of at least 81% KCl concentration a modification function of the form $\sin(\pi Q/Q_{\text{max}})/(\pi/Q_{\text{max}})$ was used prior to transformation, where Q_{max} is the upper limit for the integration in equation (2). Q_{max} was 18 Å⁻¹ for these transforms. This has the effect of reducing ripples in $G(r)$, which arise from truncation of the data and noise at high Q . However, it also reduces the resolution in real space due to convolution with a peak function which has a full width of $5.44/Q_{\text{max}}$ (Windsor 1981).

4. Principal features of the data

As mentioned previously, the interpretation of the structure factors and distribution functions for these mixtures has been aided by the availability of the partial structure factors for the two pure salts. In particular, the distinctly different characteristics of the two salts facilitate the identification of features in the mixture. One such readily

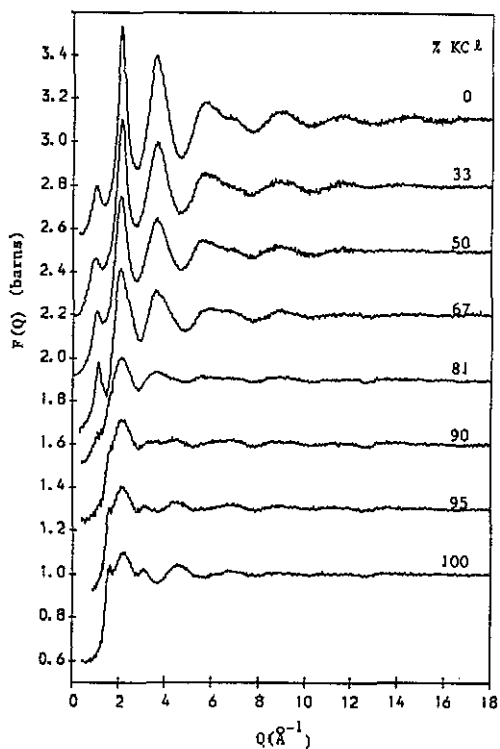


Figure 1. Total structure factors for all of the concentrations studied. Successive plots are displaced by 0.3.

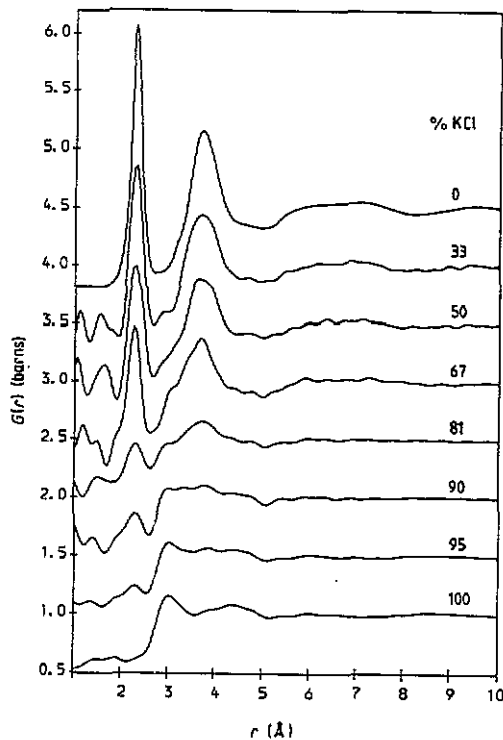


Figure 2. Total distribution functions for all the concentrations studied. Successive plots are displaced by 0.5.

distinguishable feature is the sharp principal peak in $g_{\text{ZnCl}}(r)$ at $r = 2.3 \text{ \AA}$. No other pair of ions in this three-component system can be expected to approach this close; so the peak at this position in the total $G(r)$ functions for these mixtures has been identified with this partial. The chlorine-chlorine partial $g(r)$ is the major contributor to the total $G(r)$ for all the samples studied. The form of this partial for pure ZnCl_2 is markedly different from that for KCl . The first peak at $r = 3.7 \text{ \AA}$ is clearly identifiable for pure ZnCl_2 and its subsequent behaviour with increasing KCl concentration can be followed.

From the Fourier transforms the structural parameters listed in table 2 have been obtained. The coordination numbers of anions about a cation have been determined by the integration of $4\pi\rho_0r^2G(r)$ to the first minimum following the principal peak. These values are fairly well determined since the minimum following the first $g_{\text{ZnCl}}(r)$ peak remains deep for all the mixtures for which this peak has been observed.

The effects of truncation and noise in the data, even when a modification function was used, meant that the direct Fourier transform contained structure in its low- r region due to transformation artefacts. This is particularly significant for the mixtures of low zinc concentration, since it means that little information is obtainable from a direct Fourier transformation. In order to extract information in the low- r region, fits to the structure factor data were obtained using the maximum entropy technique for the mixtures with 66.7%, 81%, 90%, 95% and pure KCl concentrations. This method of extracting information from noisy data is described by Skilling and Bryan (1984) and the algorithm outlined therein was the one that was used. Since the method involves fitting

Table 2. Structural parameters for the Zn-Cl peak for the zinc chloride and potassium chloride mixtures.

	Position (Å)	Scaled height	Width (Å)	Coordination number
Pure ZnCl				
330 °C	2.28 ± 0.01	8.9 ± 0.2	0.26 ± 0.01	3.93 ± 0.06
600 °C	2.29 ± 0.01	7.5 ± 0.3	0.33 ± 0.01	3.67 ± 0.07
33.3% KCl				
340 °C	2.281 ± 0.004	9.5 ± 0.2	0.26 ± 0.01	4.2 ± 0.1
450 °C	2.278 ± 0.007	9.0 ± 0.3	0.27 ± 0.01	3.9 ± 0.1
50% KCl				
340 °C	2.26 ± 0.01	8.6 ± 0.8	0.26 ± 0.02	4.1 ± 0.1
450 °C	2.279 ± 0.007	8.4 ± 0.4	0.30 ± 0.02	3.84 ± 0.10
66.7% KCl				
Inverse transform	2.28 ± 0.02	11.7 ± 0.4	0.28 ± 0.02	3.9 ± 0.1
Maximum entropy	2.26	10.5		
81% KCl				
Inverse transform	2.28 ± 0.03	12 ± 1	0.43 ± 0.05	4.1 ± 0.2
Maximum entropy	2.30	8.3		
90% KCl				
Inverse transform	2.31 ± 0.04	13 ± 2	0.48 ± 0.05	4.7 ± 0.3
Maximum entropy	2.24	11.6		
95% KCl				
Maximum entropy	2.29	16.8		

to Q -space data, by transformation from real space, truncation effects are minimized. Furthermore, since the maximum-entropy method does not introduce correlations into the final solution other than those required by the data, any feature observed in the solution can be regarded as arising from the data and not from transformation artefacts. The entropy of the solution is measured with reference to a default level, for which the entropy of the solution would be a maximum in the absence of any data. For those $G(r)$ functions in figure 3 this default level is $G(r) = 1$ for all r . Any departure from this uniform level represents real information. These maximum-entropy solutions show a clear contribution from the principal peak in g_{ZnCl} at $r \approx 2.3$ Å even for the 95% KCl concentration mixture. It should, however, be noted that, whereas the use of a modification function produces a known convolution effect upon $G(r)$, the effect of using the maximum-entropy method is less well defined. As a result the usefulness of the method for obtaining quantitative information from $G(r)$, such as peak sizes and coordination numbers, is limited. The method does prove useful, however, for identifying real structural features in $G(r)$ that would otherwise be obscured by transformation artefacts.

The first diffraction peak, subsequently referred to as the 'pre-peak', observed at 1.01 Å⁻¹ in the total structure factor of ZnCl_2 has been identified by Biggin and Enderby, using isotopic substitution of chlorine, to originate from S_{ZnZn} . Numerous other molten 2:1 salts exhibit this same feature. Studies of these systems have universally shown that it is the cation species alone which gives rise to this 'pre-peak' (e.g. MgCl_2 by Biggin *et al* (1984) and the nickel halides by Wood and Howe (1988)). The positions and heights

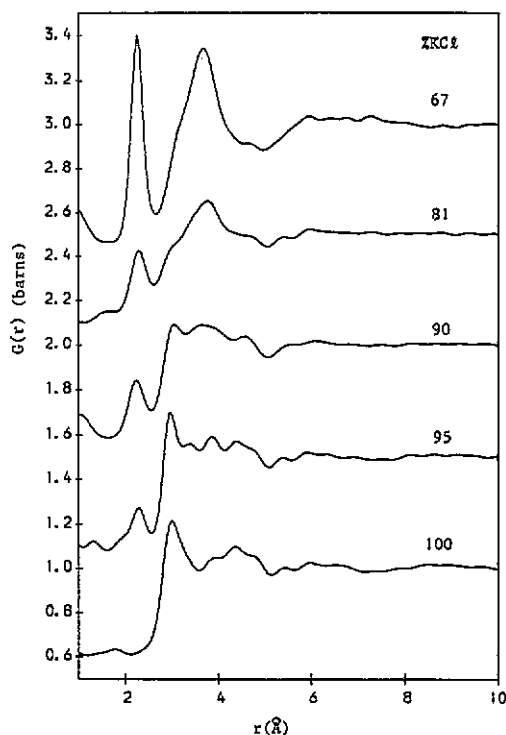


Figure 3. Maximum-entropy solutions to fit the high KCl concentration structure factor data. Successive plots are displaced by 0.5.

Table 3. Pre-peak parameters for the zinc chloride and potassium chloride mixtures.

	Position (\AA^{-1})	Height	Scaled height
Pure ZnCl_2			
330 °C	1.005 ± 0.01	0.140 ± 0.008	3.9 ± 0.2
600 °C	0.94 ± 0.01	0.13 ± 0.01	3.6 ± 0.3
33.3% KCl			
340 °C	1.00 ± 0.02	0.098 ± 0.008	4.9 ± 0.4
450 °C	0.98 ± 0.02	0.11 ± 0.01	5.4 ± 0.5
50% KCl			
340 °C	1.05 ± 0.02	0.109 ± 0.009	8.4 ± 0.7
450 °C	1.03 ± 0.02	0.12 ± 0.01	9.5 ± 0.8
66.7% KCl			
450 °C	1.10 ± 0.02	0.17 ± 0.01	25 ± 2
81% KCl			
820 °C	1.12 ± 0.03	0.026 ± 0.02	11 ± 8

of this diffraction peak are listed in table 3 for all the $\text{ZnCl}_2 + \text{KCl}$ mixtures for which it has been observed. In addition, the heights scaled by the coefficient for S_{ZnZn} are also listed. It is clear that the peak does not disappear as potassium chloride is added up to a concentration of 66.7% KCl. Furthermore, if it is assumed that this peak still arises

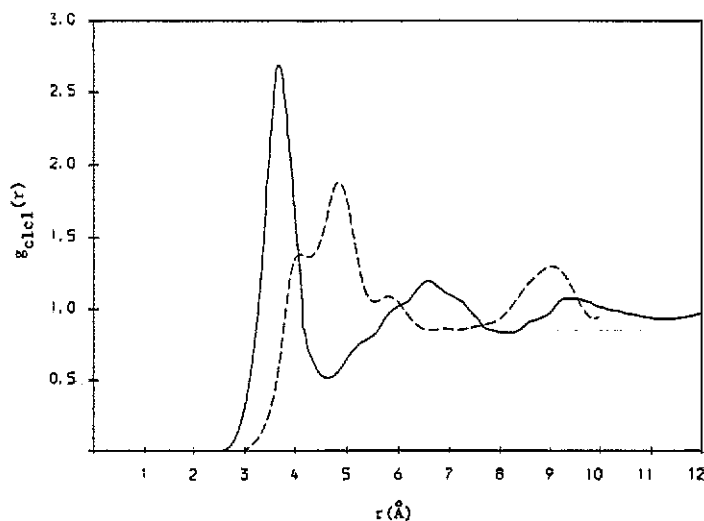


Figure 4. The chlorine-chlorine partial distribution functions for pure ZnCl_2 (—, from Biggin and Enderby (1981)) and pure KCl (---, from Derrien and Dupuy (1975)).

solely from the S_{ZnZn} contribution and account is taken of the diminishing zinc concentration, this peak in the partial structure factor must be enhanced at high KCl concentrations. It is still visible as a small shoulder for the 81% solution, although its magnitude for this $F(Q)$ is not well determined. There is also a small but significant shift to higher Q with increasing KCl concentration and to lower Q with increasing temperature, as expected from thermal expansion.

5. Discussion

5.1. The Cl-Cl structure

From the partial structural investigations it is known that the anion structures of the two pure salts are very different from one another. For example, in ZnCl_2 the mean nearest-neighbour Cl-Cl distance is 3.71 Å with a coordination number of 8.6 ± 0.5 (Biggin and Enderby 1981), whereas for KCl these figures are 4.8 Å and 14 respectively (Derrien and Dupuy 1975). The chlorine-chlorine partial distribution functions for the two pure salts are reproduced in figure 4. For all the mixtures studied, the Cl-Cl partial contributes at least 52% of the total coherent scattering and therefore dominates the total structure factors. The structure factors and distribution functions for the mixtures with KCl concentrations up to 66.7% closely resemble those of pure ZnCl_2 as opposed to those of pure KCl. This suggests that the short-range anion structure found in molten ZnCl_2 is the dominant structure up to this KCl concentration. Beyond this concentration, the real space functions show that contributions from the nearest-neighbour g_{ClCl} peak at 3.7 Å are still present, but in addition the g_{ClCl} peak appropriate to KCl emerges at 4.8 Å as we move towards pure KCl.

As a means of determining the extent of the chemical interaction between the two salts, attempts were made to model the total structure factors and distribution functions

Table 4. Contributions made by the partial structure factors $S_{\text{ClCl}}(Q)$ from the ZnCl_2 and KCl pure salt structures, to the total $F(Q)$ model fits in figure 4.

	Total Cl-Cl coefficient	In proportion to salt concentration		Values used for fits	
		ZnCl_2	KCl	ZnCl_2	KCl
33.3% KCl	0.3584	0.2867	0.0717	0.304	0.054
50% KCl	0.3303	0.2202	0.1101	0.244	0.086
66.7% KCl	0.2992	0.1496	0.1496	0.189	0.111

by recombining the partial components for the pure salts according to equation (1). The expression for the recombined total structure factors is

$$\begin{aligned}
 F(Q) = & C'_{\text{KK}}[S_{\text{KK}}(Q) - 1] + C'_{\text{ClCl}}[S_{\text{ClCl}}(Q) - 1] + C'_{\text{ZnZn}}[S_{\text{ZnZn}}(Q) - 1] \\
 & + C'_{\text{KCl}}[S_{\text{KCl}}(Q) - 1] + C'_{\text{ZnK}}[S_{\text{ZnK}}(Q) - 1] \\
 & + C'_{\text{ZnCl}}[S_{\text{ZnCl}}(Q) - 1] + 1
 \end{aligned}$$

where the $C'_{\alpha\beta}$ refer to the coefficients for the partials $S_{\alpha\beta}$ listed in table 1 for each mixture. Only the $S_{\text{ZnK}}(Q)$ term is unknown but this is never more than 3.2% of the total coherent scattering. Because of the dissimilarity of the anion structures of the two pure salts, two quite different chlorine structures are available for modelling the data, which was fitted in the following way. Each $F(Q)$ was reconstructed using a combination of the partial components and a mixture of the two chlorine-chlorine partials ($S_{\text{ClCl}}[\text{ZnCl}_2]$ and $S_{\text{ClCl}}[\text{KCl}]$) with coefficients appropriate to the zinc and potassium concentrations. These clearly did not fit the data, as there was too large a contribution from the $S_{\text{ClCl}}[\text{KCl}]$ and too little from $S_{\text{ClCl}}[\text{ZnCl}_2]$. It was found that for the 33.3%, 50% and 66.7% KCl concentration mixtures, the best fits could be obtained if the contributions from $S_{\text{ClCl}}[\text{KCl}]$ were reduced to 0.76 times what they should be if weighted by the proportion of chlorine from the potassium chloride in these mixtures. The $S_{\text{ClCl}}[\text{ZnCl}_2]$ contributions were increased accordingly, so that the total $S_{\text{ClCl}}(Q)$ contributions from both sources were what they should be according to the coefficients of table 1. The coefficients used are listed in table 4, and the model fits obtained are shown in reciprocal space and real space in figures 5 and 6, respectively. The model was in poor agreement with the data for the highest KCl concentration mixtures owing, at least in part, to the poor quality of the original partials for molten KCl.

One must conclude from this modelling that the influence of the zinc ions on the anion structure remains dominant to high KCl concentrations. More directly, the Cl-Cl partial structure factor, and further information on the Zn-Cl and K-Cl partials, could be obtained from a chlorine isotopic substitution experiment. This would enable us to determine the extent to which the anion structure is modified without recourse to a model using linear combinations of the two pure salt Cl-Cl functions.

5.2. The Zn-Cl structure

The Fourier transforms in figure 2 and the maximum-entropy solutions in figure 3 reveal that a contribution from the principal peak in $g_{\text{ZnCl}}(r)$ at $r = 2.3 \text{ \AA}$ is distinguishable for

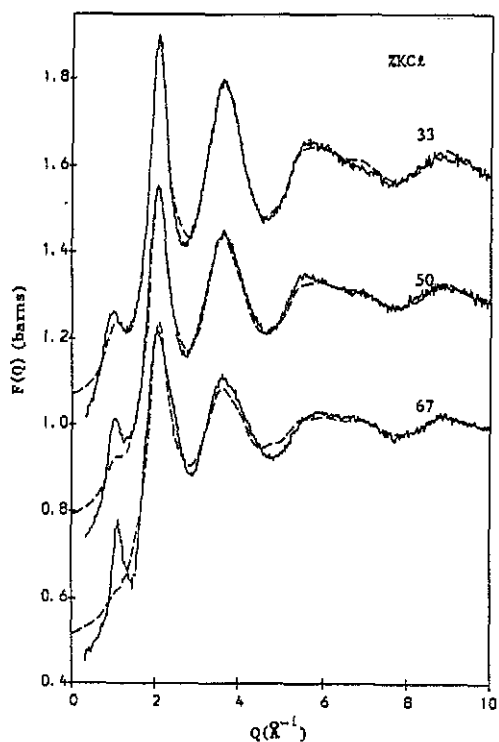


Figure 5. The total structure factors for the 33%, 50% and 67% mixtures (—), compared with the recombined partials (---). These were recombined according to the coefficients given in tables 1 and 4.

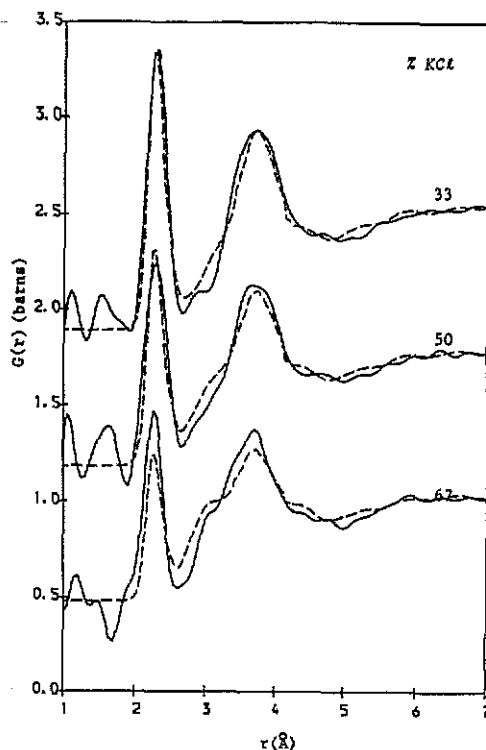


Figure 6. The total radial distribution functions for the 33%, 50% and 67% mixtures (—), compared with the recombined partials (---). These were recombined according to the coefficients given in tables 1 and 4.

all the mixtures including those with high KCl concentrations. Moreover, a coordination number of four anions around each zinc ion is retained to high KCl concentrations. This is contrary to the suggestions of Ellis (1966) and Itoh *et al* (1982) that the species ZnCl_3^- and ZnCl_2 are formed. The height of this peak, when scaled according to the coefficient of the Zn-Cl partial contribution, and its persistence up to high KCl concentrations indicates that the ZnCl_4 structural unit is very stable in these mixtures. Indeed the persistence in these mixtures of the local Cl-Cl structure pertaining to ZnCl_2 , represented by a fixed Cl-Cl distance and a constant ratio of nearest-neighbour Cl-Cl to Zn-Cl distances, shows that the arrangement of chloride ions around zinc ions remains tetrahedral.

Duke and Fleming (1957) proposed from their electrical conductivity measurements of $\text{ZnCl}_2 + \text{KCl}$ mixtures that K^+ ions dominate the conduction. The formation of isolated and stable ZnCl_4^{2-} units, leaving K^+ ions relatively free, is consistent with this proposal and ought to give rise to a sharpening up of the principal peak in g_{ZnCl} , since there would be no external constraints upon the structure of the tetrahedra through corner linking to others. Experimental evidence for this is somewhat inconclusive. The scaled height of this peak appears to remain constant upon addition of KCl but is observed to have significantly increased relative to that in pure ZnCl_2 at a concentration

of 67% KCl. Unfortunately its height and width become increasingly uncertain at higher KCl concentrations.

5.3. The K-Cl structure

From the investigation of Derrien and Dupuy (1975) the first two peaks in the total $G(r)$ for pure KCl can be attributed to the first peaks in g_{KCl} at 3.1 Å and g_{ClCl} at 4.8 Å. The height of the peak at 3.1 Å drops rapidly as ZnCl_2 is added to KCl. In addition, the models in figure 5 show a poor agreement in real space over the region of 2.6–3.4 Å for the salt mixtures, with the observed $G(r)$ being lower in this region than that of the model. This is the region of the main peak in g_{KCl} for pure KCl and the model indicates a loss of K-Cl structural ordering consistent with enhanced K^+ ion mobility.

In contrast with the stability of the zinc chloride structure, the structure of potassium chloride is greatly modified by the addition of only 5–10% of zinc chloride. This is clearly evident from both Q -space and real-space functions, with the main peak in $g_{\text{KCl}}(r)$ being substantially reduced in height and the anion structure being considerably modified by the formation of ZnCl_4^{2-} tetrahedral complexes.

5.4. Intermediate-range order

The persistence of intermediate-range ordering between cations across the composition range of the mixtures, as evidenced by the 'pre-peak', seems difficult to reconcile with the suggested network-breaking role of the alkali halide. Before attempting to explain the observed behaviour, it is useful to consider the nature of this ordering in pure ZnCl_2 .

The structure of molten ZnCl_2 has been simulated by McGreevy and Pusztai (1990) using the 'reverse Monte Carlo' method. From their model, they observed that the occupied tetrahedral sites were clustered together, forming regions of high and low zinc ion concentration. These clusters were linked by . . . Zn-Cl-Zn . . . chains. They concluded that the cation density fluctuations (on a scale of 5–10 Å) were the origin of the intermediate-range ordering and the source of the cation 'pre-peak'.

The observed behaviour of the structure factor for these mixtures up to 67% concentration can be explained if the KCl does not act as a network breaker within these clusters, but rather between them, forming regions of high potassium ion concentration with a local anion structure appropriate to that found in pure KCl. These potassium ion density fluctuations could then result in an additional contribution to the 'pre-peak' from $S_{\text{KK}}(Q)$. This is consistent with the observed persistence of this peak in the total structure factors and its enhancement for the 67% KCl mixture, as well as the apparent admixture of the two anion structures.

Direct experimental confirmation of an $S_{\text{KK}}(Q)$ contribution is made difficult by the absence of suitable potassium isotopes for substitution. However, from the Raman scattering results of Ellis, LiCl is believed to behave in a similar structure-breaking manner. Using $\text{ZnCl}_2 + {}^7\text{LiCl}$ mixtures, one should be able to determine whether or not the alkali metal is playing such a role in the intermediate-range ordering. ${}^7\text{Li}$ has a scattering length which is significantly smaller in magnitude than that of potassium, and any contributions to the 'pre-peak' from $S_{\text{LiLi}}(Q)$ would be correspondingly reduced.

6. Summary

From our results it has been seen that the structure of molten zinc chloride, at both short and intermediate range, is not readily perturbed by the addition of a 'structure-breaking'

alkali chloride. This is a consequence of the strong preference for the zinc ion to be tetrahedrally coordinated by chloride ions. In contrast, the structure of potassium chloride is greatly modified by only a few per cent of zinc chloride, as the zinc ions disrupt the anion structure by seeking their own preferred environments. The zinc ion dominates the anion structure rather than the potassium ion. More detailed information on the local cation environments (e.g. from EXAFS studies) would be useful in quantifying the way in which the pure salt structure has been modified.

The persistence and enhancement of the 'pre-peak' is consistent with the clustering model proposed by McGreevy and Pusztai for the origin of medium-range ordering in zinc chloride.

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