A VIEW AND A REVIEW OF THE MELTING OF ALKALI METAL HALIDE CRYSTALS
Part 2. Pattern of eutectics and solid solutions in binary common ion mixtures

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A representational model, proposed to account for the physical changes that accompany the melting of alkali halides, was described in Part 1 [1]. The liquid is portrayed as undergoing continual dynamic structural reorganization of its constituent ions between individual small domains, zones of various regular, crystal-type arrays. These alternative arrangements are stabilized by the enthalpy of melting, which, in liquids, relaxes the restriction for solids that only the single, most stable, crystal structure can be present. The dynamic character of the melt accounts for its fluid character and the loss of long-range order [1, 2]. This model is extended here to consider the phase diagrams of binary, common ion, alkali halide mixtures comprehensively reviewed in [3]. Factors determining whether each of these yields a eutectic, or a solid solution, on cooling are discussed and several trends in the 70-phase diagrams are identified. Eutectic formation, involving maintenance of the liquid state below the melting points of the pure components, is ascribed to the participation, in an extended dynamic equilibrium, of additional domains having the regular structures characteristic of double salts. The known crystalline double binary halides [3], Li/Cs or Rb/F, Cl, Br or I, melt at temperatures well below those of the simpler pure component salts. It is concluded that the set/liq model for melting, proposed in [1, 2], accounts for some important properties of the phase diagrams presented in [3].

Keywords: binary alkali halide mixture melting, eutectic formation, fusion, melting, solid solution formation

Introduction

Melting is a first order physical change which, however, lacks a generally accepted theoretical and representational explanation, though many alternative models have been proposed to account for this most familiar of phenomena. In Part 1 [1], the (relatively small) density and energy changes associated with the fusion of alkali halides were comparatively compared and quantitatively analyzed. From the trends recognized for these particularly well-defined salts, it was concluded that, on passing through the melting point, T_m, there were only restricted, and perhaps specific, changes in the regular structural dispositions of ions within local arrays, accompanied by the loss of long range order. To account for the observations, it was suggested that the melt formed at T_m is composed of arrangements of ions that conform to one or more of the regular packing structures that are characteristic of crystalline (ionic) solids. This is referred to as the set/liq model [1, 2]. The melt is envisaged as being composed of small domains of regular crystal lattice-type dispositions of ions (regliq), coherently bonded through electrostatic interactions between neighbours, which are strong but are not oriented. Contiguous regions, within each of which there is locally regular order, are separated by interfaces characterized by less regular (irregliq) material. The available energy within the composite assemblage, a matrix of regular zones, maintains the constant interconversion of material, through transfer of ions between the alternative structures present. This rapid dynamic equilibration accounts for the density of the melt, where strong interionic forces are regarded as imposing local order. Throughout the greater proportion of the melt, the network of irregliq contacts, interfaces between domains within which there is lesser order and enhanced freedom of ionic motion, accounts for overall fluidity and absence of long range order in the liquid which gives no sharp X-ray diffraction pattern. The enthalpy of fusion, ΔH_F, is identified as providing the additional energy required to stabilize the dynamic and less ordered zones that separate the individual regular domains in the melt. This energy is also regarded as relaxing the restriction that only the single most stable structural arrangement can be present, an intrinsic attribute of each crystalline solid. Progressive heating above the T_m is expected to increase the proportion of irregliq material present thereby enhancing the freedom of motion of the individual constituents (anticipating the later, and again discontinuous, further enhancement of freedom of movement on volatilization, to form a gas).

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Eutectic-forming mixtures are characterized by their ability to remain liquids at temperatures below the melting point, T_m, of one, often more, of the components. Variations of composition ranges of stable melts with temperature are represented by phase diagrams. In the present paper, the set of 70-phase diagrams reported by Sangster and Pelton [3], for all the binary alkali halide mixtures that contain either a common cation or a common anion, are comparatively examined. The analysis was undertaken to determine whether the patterns of behaviour observed are consistent with the set/liq melting model, Part 1 [1] and [2]. The survey [3] is an exceptionally thorough and critical appraisal of the literature available, citing 332 sources to 1986. Within this wealth of information, trends of melting point variations with composition have been recognized, which are here identified as being consistent with the dynamic set/liq model for melts [1, 2]. While the information upon which this comparative analysis is based [3] contains some limitations, the overall pattern of agreement is regarded as exhibiting sufficient significant and valuable positive evidence to merit recommendation of the approach as potentially capable of extending both theory and understanding of melting. Interest in solid–liquid equilibria of diverse binary mixtures has continued in the recent literature [4–7].

Phase diagrams

Dominant features of the phase diagrams presented, and critically discussed, by Sangster and Pelton [3] are summarized in Tables 1 and 2: the 70 binary alkali halide systems each contain one common ion. Also included in these Tables are some additional thermochemical data from [8]. The form of each melt-composition curve given in [3] is principally distinguished by whether the mixture forms a eutectic (E) or a solid solution (SS). As explained by the authors, the data used in 'obtaining a «best» evaluated phase diagram', was acquired from a diverse range of sources and not all conclusions can be entirely precise and unambiguous. Nevertheless, a high degree of consistency was achieved overall. Two of the 40 entries in Table 1 and five from the 30 systems in Table 2, marked (*), were regarded [3] as based on insufficient experimental evidence and consequently conclusions drawn therefrom are less reliable.

Tables 1 and 2 provide the background information from which the physical and chemical trends discussed below were identified and this framework provides a context for presentation of the patterns discerned. The common ions in each mixture form the columns and the binary combinations of the different ionic components are listed in rows with the volume ratios for the ion pairs (bracketed in the first column)

Table 1 Form of each phase diagram for common anion binary mixtures of alkali halides (data from Sangster and Pelton [3]), including also calculated lattice potential energy (U_{POT}) differences and (ratios) for crystalline components, from [8]

Cations in mixture (CVR)	Common anion			
	fluoride	chloride	bromide	iodide
lithium/cesium (0.0943)	E, C 286 (1.384)	E+P, C(2) 177 (1.269)	E+P, C 156 (1.247)	E, C* 130 (1.217)
lithium/rubidium (0.125)	E+P, C 256 (1.331)	E+P, C 154 (1.226)	E+P, C 137 (1.210)	E+P, C 113 (1.183)
lithium/potassium (0.167)	E 222 (1.275)	E 133 (1.190)	E 117 (1.174)	E 98 (1.155)
sodium/cesium (0.228)	E 166 (1.223)	E 112 (1.170)	E 100 (1.158)	E 82 (1.137)
sodium/rubidium (0.302)	E 136 (1.176)	E 89 (1.131)	E 81 (1.124)	E 65 (1.105)
sodium/potassium 0.404	E 102 (1.126)	SS, LTS 68 (1.097)	SS, LTS 61 (1.091)	SS, LTS 50 (1.079)
lithium/sodium 0.414	E 120 (1.132)	SS 65 (1.084)	SS, LTS 56 (1.076)	SS* 48 (1.070)
potassium/cesium (0.546)	E(+SS, 25%) 64 (1.086)	SS 44 (1.067)	SS (+E, small) 39 (1.062)	E(+SS, 35%) 32 (1.053)
potassium/rubidium (0.748)	SS 34 (1.044)	SS 41 (1.031)	SS 20 (1.031)	SS 15 (1.024)
rubidium/cesium (0.754)	SS 30 (1.040)	SS 27 (1.035)	SS (+E, small) 19 (1.030)	SS (+E, small) 17 (1.028)

Evidence from phase diagrams in [3] identifies the solidified products as forming E – eutectic, P – peritectic or SS – solid solution: also there may be C – compound formation (crystalline double halide) or LTS – low temperature separation of individual component salts from a eutectic. Numbers give the difference (AX–BX) and (in brackets) the ratio (AX/BX) of calculated total lattice potential energy values, U_{POT}/kJ mol^{-1} [8], for the components of each mixture; *for these two mixtures the literature data available were limited in extent and/or ambiguous in interpretation [3] and the results are, therefore, less reliable; CVR – cation volume ratio

Table 2 Form of each phase diagram for common cation binary mixtures of alkali halides (data from Sangster and Pelton [3]), including also calculated lattice potential energy (U_{POT}) differences and (ratios) for crystalline components, from [8]

Anions in mixture (AVR)	Common cation				
	lithium	sodium	potassium	rubidium	cesium
fluoride/iodide (0.221)	E 300 (1.411)	E 228 (1.332)	E 176 (1.278)	E* 157 (1.254)	E 144 (1.240)
fluoride/bromide (0.312)	E 242 (1.307)	E 178 (1.243)	E 137 (1.204)	E 123 (1.189)	E 112 (1.177)
fluoride/chloride (0.370)	E 196 (1.235)	E 141 (1.183)	E 107 (1.153)	E 94 (1.138)	E* 87 (1.132)
chloride/iodide (0.557)	E 104 (1.142)	E(+SS, 25%) 87 (1.128)	E(+SS, 45%) 69 (1.109)	E*(+SS?) 63 (1.102)	E/SS? 57 (1.095)
bromide/iodide (0.707)	SS* 58 (1.079)	SS 50 (1.073)	SS 39 (1.062)	SS 34 (1.055)	SS 32 (1.053)
chloride/bromide (0.778)	SS* 46 (1.058)	SS 37 (1.051)	SS 30 (1.045)	SS 29 (1.045)	SS 25 (1.040)

Evidence from phase diagrams in [3] identifies the solidified products as forming E – eutectic or SS – solid solution. Numbers give differences (*MX*–*MY*) and (in brackets) ratios (*MX/MY*) of the calculated total lattice potential energy values, U_{POT}/kJ mol^{-1} [8], for the components of each mixture; *for these five mixtures the literature data available were limited in extent and/or ambiguous in interpretation [3] and the results are, therefore, less reliable; AVR – anion volume ratio.

increasing downwards. (Here cation and anion volume ratios, CVR or AVR respectively, are the preferred parameters for ionic size comparisons.) The thermodynamic data in Tables 1 and 2 are the differences (kJ mol^{-1}) and ratios (bracketed) of calculated total lattice potential energies [8] for the pure crystalline salts in each mixture. These trends show that eutectics (E) are formed when there are significant differences in the sizes of the varied ion constituents (for both anions and cations) in the different mixtures: more closely comparable sizes of cation pairs or of anion pairs form solid solutions (SS). The transition between E and SS is not sharp and there are examples of intermediate behaviour. For four mixtures, labelled LTS in Table 1, cooling initially yields solid solutions, but these separate into the individual constituents at lower temperatures.

The alternative formation of E or SS phases on cooling is controlled by factors in addition to the CVR or AVR. Mixtures containing fluoride as the common ion, with Na/K, Li/Na and (possibly) K/Cs, form eutectics, whereas with the other halides (Cl, Br or I) there is a tendency towards SS formation, Table 1. Similarly, a eutectic is formed from the Cl/I anion combination with Li, whereas with the other alkali metal cations these mixtures tend to form solid solutions, Table 2. It is concluded, therefore, that eutectic formation tends to occur in those mixtures that contain the smallest common ions, Li$^+$ or F$^-$. Moreover, cation mixtures having the greatest size differences, Li$^+$/Cs$^+$ and Li$^+$/Rb$^+$ (CVR values 0.0943 and 0.125, respectively), form stable crystalline double salts with all four anions. Anion mixtures form no such binary halide crystalline phases: possibly because the smallest AVR, 0.221 for F$^-$/I$^-$, is relatively larger.

Common anion systems (Table 1)

Eutectics are formed by those binary common ion mixtures for which the difference in total lattice potential energies, U_{POT} [8], of the individual constituent salts ($U_{AX} - U_{BX}$) is greater than 65 kJ mol^{-1} and the ratio (U_{AX}/U_{BX}) is greater than 1.086. Solid solutions are formed when the difference is less than 63 kJ mol^{-1} and the lattice energy ratio is below 1.084. Binary solid solutions are formed when CVR values are greater than 0.3, except with the fluorides, which form eutectics in those mixtures for which the CVR values are less than about 0.6. Several mixtures, however, show intermediate behaviour [3]. Four systems that can alternatively be regarded [3] as eutectics (shown as SS on Table 1) are: Na/K/Cl, Br or I and Li/Na/Br; these form solid solutions which separate at lower temperatures (LTS in Table 1), significantly below the melting points of the mixtures [3]. In some other mixtures, K/Cs/Cl, Br or I, there is significant mutual solubility of solid components and some evidence of eutectic formation. In contrast, neither lattice energy differences nor ratios could be associated with the formation of the crystalline double salts (possibly all Li/Cs and Li/Rb halides) and no range of energy values in Table 1 correlates with LiCsX$_2$ or LiRbX$_2$ formation.

Common cation systems (Table 2)

Eutectics were (also) formed by all those common cation binary systems [3] with differences in lattice potential energy values, (U_{MX}–U_{MY}), greater than 65 kJ mol^{-1} and ratio values, (U_{MX}/U_{MY}) above 1.086. Below these magnitudes, SS were formed. This pat-

tern of behaviour, including the transition values, is identical with that found for the common anion mixtures. Again, the borderline region, here the Cl^-/I^- mixtures, is characterized by appreciable mutual solubility of the constituents and ambiguities arise in classifying the phase diagrams into either of the types distinguished, E or SS.

Comment

It is concluded that the lattice energy difference (U_{POT}) for the pure salt constituents of each binary, common ion, mixture melt is the dominant factor in determining whether the solid formed on cooling is composed of separate microcrystals of the individual components (E) or forms a solid solution (SS). If the difference of the lattice stabilities for the pure crystalline components of the mixture is (about) 65 kJ mol^{-1} or more, separation of the two salts occurs (E) but, with a smaller difference, the SS is formed. This is a considerable energy difference, much greater than is represented by the entropy of simple unmixing and up to three times the heats of fusion, evidence of the considerable stabilities of these mixtures. The intermediate zones of Tables 1 and 2 include significant ranges of mutual solubilities, with the formation of metastable solid solutions, some undergoing kinetic-controlled component separation at relatively low temperatures [3] (LTS).

Uncertainties in these comparisons include the use of lattice energy values for standard conditions, rather than at T_m. Comparisons of fusion enthalpies identified no significant trends. A further complication is that, whereas most alkali halides crystallize in 6:6 coordination, CsBr, CsI and (below 742 K) CsCl exhibit 8:8 coordination.

From the phase diagrams in [3], the following dominant features were recognized.

Double salt formation

Binary crystalline compounds are formed only from the common anion combinations for which the CRV values are small, Cs/Li (0.0943) and Rb/Li (0.125) and (probably) include all four anions, F, Cl, Br or I. Mutual solubilities of the salts in these mixtures are small, most are 2–3%.

Eutectic formation

Eutectics were formed in binary common ion mixtures for which the AVR or CVR values were small, less than 0.3, though the range extended to about 0.6 for mixtures containing the smallest common ions (Li^+, F^-). Eutectic formation was observed only in those mixtures of ionic solids for which the lattice po-

tential energy values were relatively different, i.e., greater than about 65 kJ mol^{-1}.

Comprehensive solid solution formation

Solid solutions were formed when the AVR or CVR values and stabilities of the component salts were more nearly comparable. Some mixtures, exhibiting significant mutual solubilities of constituents, were difficult to classify and other solid solutions underwent separation of components at lower temperatures, LTS in Table 1.

Change of melting point with mixture composition

Binary, common ion, alkali halide mixtures remain in the liquid state at temperatures below the T_m of one, or often of both, pure components [3]. A principal objective of the present survey was to characterize quantitatively the pattern of behaviour observed and, where possible, to provide a theoretical explanation. One measure of the ability of (added) Salt B to depress the T_m of Salt A in the mixture is the slope of the line joining the T_m of Salt A to the eutectic point on the phase diagram. This line represents the progressive changes in composition of the liquid mixture with temperature during the separation of Salt A during cooling. For some of the eutectic-forming systems reviewed in [3], the (molar) composition-T_m line is (almost) straight and for others there is a pronounced curve, which often tends to increase in slope as the eutectic is approached. In those mixtures that form solid solutions, the rates of change of T_m with composition tend to be relatively less than those which yield eutectics.

In the present comparative analyses of the phase diagrams in [3], it has been found convenient to discuss behaviour patterns through the relative magnitudes of two measured slopes for each T_m-eutectic line, Fig. 1. The initial Slope, I, represents the rate of T_m diminution close to pure Salt A that results from the addition of small amounts of Salt B: for some mixtures this constant value may extend to the eutectic. The final Slope, F, represents the maximum rate of T_m change with composition: for the systems in [3] these measured values of F refer to compositions in the approach to the eutectic. Usually F is significantly greater than I for mixtures that form a eutectic but for solid solutions, the Slope F may be less than Slope I. Each slope reported in Table 3 is the (measured) temperature difference (ΔT/K) that corresponds to a 1% change of molar composition: i.e., from (x%Salt A+(100–x)%Salt B) to ((x+1)%Salt A +(99–x)%Salt B). Slope I was the average measured for 0–5% molar additions of Salt B and Slope F applied across a similar composition interval in the approach to

the eutectic mixtures. Results from the binary halide phase diagrams given in [3] are summarized in Table 3.

The measured values of Slope *I* and of Slope *F* reported and discussed here are subject to several uncertainties, some of which are discussed in greater detail in [3]. Moreover, the reliability of data differ between the various systems. For some phase diagrams [3], the measurements available are insufficient to define the phase relationships with certainty (*). Other comparisons of reports reveal ambiguities between data obtained from different sources. The measurement of slopes from the phase diagrams in [3] introduces some further error, which may have been minimized, but not eliminated, by the use of consistent criteria. These appreciable errors limit, to some extent, data interpretation. Nevertheless, despite these shortcomings and uncertainties, the general trends reported below, and regarded as significant, have been recognized.
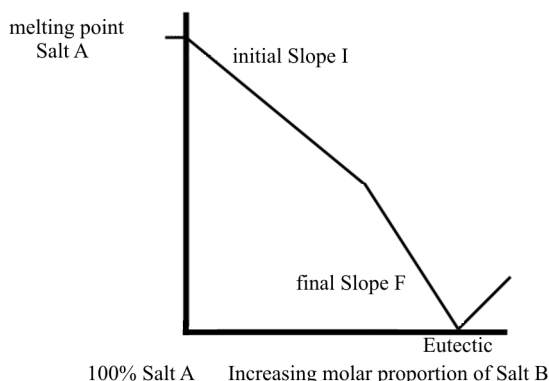
Notes for Table 3

Data from the phase diagrams of [3] have been classified into groups A to H, for which Slope *I* and Slope *F* values in each set decrease within similar ranges of magnitudes. The mixture compositions of each group, together with features that characterize each behaviour type distinguished, are given in 'Common anion binary mixtures' and 'Common cation binary mixtures'. Because the data show appreciable variations, and for reasons outlined above, these limits (given as root mean square deviations) have been included in Table 3. Overall limiting values of Slopes *I* and *F* for each Group are reported in Columns 3 and 6. However, because a small proportion of such values were either much larger or smaller than the mean, the range of values representing 75% of the measurements is

Fig. 1 Phase diagrams: definitions of initial Slope *I*, and final Slope *F*, used in text discussions. For most alkali halide binary mixtures giving eutectics [3] the T_m-composition lines (omitted from this diagram) are curved, concave downwards

Table 3 Summary of magnitudes of initial (*I*) and final (*F*) Slopes (defined in text) from common ion binary phase diagrams for the alkali halides in [3]

Group (number of mixtures)	Mean initial Slope, *I*(±)	Overall range of *I* (75% range)[2]	Difference[1] values *I* (mean) (±)	Mean final Slope *F* (±)	Overall range of *F* (75% range)[2]	Difference[1] values *F* (mean) (±)
Common anion mixtures						
A (13)	4.14 (±0.50)	2.5–5.4 (3.7–4.8)	0.59 (±0.50)	9.74 (±2.06)	6.0–14.5 (7.7–11.0)	2.30 (±1.45)
B (9)	3.57 (±0.41)	2.5–4.1 (3.0–3.9)	0.35 (±0.20)	4.95 (±1.20)	2.2–8.3 (3.6–5.4)	0.96[4] (±0.87)
C (10)	2.34 (±0.65)	1.0–3.6 (1.6–2.9)	0.96 (±0.70)	2.60 (±0.91)	4.5–1.0 (1.7–3.8)	1.32 (±0.72)
D (8)	0.65 (±0.47)	0.0–1.4 (0.1–1.2)	0.50 (±0.23)	?[3]		
Common cation mixtures						
E (16)	3.70 (±0.50)	2.5–5.3 (3.2–4.5)	0.68 (±0.48)	5.40 (±1.86)	2.5–10.0 (4.3–7.7)	2.67 (±1.91)
F (4)	2.66 (±0.46)	2.2–3.3[3]				
G (5)	1.51 (±0.65)	0.7–2.3[3]				
H (5)	0.88 (±0.50)	0.5–1.7[3]				

All values refer to diminution of mixture T_m (ΔT/K) on phase diagram [3] for a 1% change of molar composition in salt mixtures; all data ranges expressed as, ±, are root mean square deviations; [1]mean differences in Slopes (*I* and *F*) for the different components (the two sides) of each phase diagram within the group; [2]overall range gives the maximum and minimum values measured, the outermost 25% are discounted in the (75% range), (bracketed), to indicate the most frequent range of magnitudes; [3]see paragraphs in text, 'Common anion binary mixtures' and 'Common cation binary mixtures', referring to groups D, F, G and H; [4]one exceptionally large value (8.0 K for NaF+CsF) was omitted from this average

also listed: outliers contributed considerably to the relatively large scatter limits (±) which are a feature of Table 3. The overall averages of Slopes I were 3.75±0.60 K (for the eutectic-forming mixtures) and 1.51±0.92 K (for the solid solutions), with closely comparable magnitudes for common cation and common anion mixtures (Table 3).

Common anion binary mixtures (Table 1)

Group A

Each of the thirteen mixtures constituting this group contains Li and forms a eutectic: Li/Cs, Rb or K/F, Cl, Br or I, together with Li/Na/F, this cation combination only formed a eutectic with F.

Phase diagrams were characterized by relatively the largest average Slopes I (4.14 K) and values of Slopes F (9.74 K) were more than twice as large. Despite some variations, individual values for these mixtures were comparable and no systematic trends with compositions were discerned. The only (apparently) anomalous line [3] was for the addition of RbF to LiF, for which the Slope I was comparatively small (2.5 K) but this was followed by an unusually large Slope F (14.5 K).

Group B

All 9 mixtures contain Na and form eutectics: Na/Cs or Rb/F, Cl, Br or I and also Na/K/F, again this cation combination only forms a eutectic with F.

The Slopes I were appreciably smaller than for the group A eutectics (3.57 K) and the magnitudes of subsequent increases (Slope F, 4.95 K) were also relatively less. No systematic trends within the values were found. The mixture Na/Rb/I was regarded [3] as borderline between E and SS and was characterized by relatively low values of the Slopes I and F.

Group C

These (10) mixtures of varied cations (CVR values 0.4–0.55) formed solid solutions on cooling: Na/Li or K/Cl, Br or I and K/Cs/F, Cl, Br or I.

Values of Slopes I (2.34 K) were below those for the eutectic forming mixtures (groups A and B) and the subsequent increases (2.60 K) were also relatively smaller. Phase diagrams were less symmetrical.

Group D

The (8) mixtures of varied cations (larger CVR values, about 0.75) formed solid solutions: Rb/K or Cs/F, Cl, Br or I.

Magnitudes of Slope I were relatively small (0.65 K) and the very small values of Slope F could not be estimated reliably for these shallow curves.

Common cation binary mixtures (Table 2)

Group E

These (16) anion combinations formed eutectics: F/Cl, Br or I/Li, Na, K, Rb or Cs, together with Li/Cl/I, the only non-fluoride mixture giving evidence of eutectic formation.

The mean magnitudes of Slopes I and of Slopes F were comparable with those of group B, though these values showed rather greater variation. The largest Slopes F (around 10 K) were for the additions LiI to LiF and NaI to NaF and all other values were appreciably lower.

Group F

These borderline mixtures (4) were difficult to classify: characteristics of both eutectic and solid solution formation were indicated for Cl/I/Na, K, Rb or Cs.

Phase diagrams were significantly asymmetrical but all shapes were comparable. For these four mixtures, Slopes I were 3.0–3.3 K for iodides added to chlorides but only 2.15–2.25 K for chlorides added to iodides. For only one line (NaI added to NaCl) was Slope F (5.6 K) greater than Slope I.

Group G

All 5 mixtures formed solid solutions (AVR–0.707): Br/I/Li, Na, K, Rb or Cs.

Phase diagrams were unsymmetrical with Slopes I for the addition of bromide to iodide varying irregularly with increasing cation size (1.70, 0.75, 0.70, 0.75, 1.60 K) and also for iodide added to bromide (2.35, 2.05, 1.45, 2.20, 1.60 K). Slopes F were comparable or smaller.

Group H

All 5 mixtures formed solid solutions (AVR–0.778): Cl/Br/Li, Na, K, Rb or Cs.

The pattern of phase diagram shapes was similar to those in group G except that Slope I values were generally less: values for the addition of chloride to bromide (1.02, 0.40, 0.70, 0.50, 0.60 K) were lower than those for bromide to chloride (1.75, 1.10, 1.20, 1.00, 0.55 K).

Double salt formation: $LiCsX_2$ and $LiRbX_2$

Crystalline double halides were either detected, or there were strong indications of their formation [3], for the binary halide (X) mixtures: LiX+CsX and LiX+RbX. Structures of seven double salts have been reported, which may (or some may not) be those present under the conditions used in the phase diagram investigations.

Burns and Busing [9] reported that $LiCsF_2$ and $LiRbF_2$ are isostructural, the Cs^+ and Rb^+ ions occupy comparable lattice sites. Li^+ is situated within F^- tetrahedra which form sheets oriented parallel to (001) and Cs^+, or Rb^+, bind the sheets together. Coordination of the larger ion is asymmetric, designated as six (Cs^+) or eight (Rb^+) and is stated to be in accordance with expectation from the anion:cation radius ratio [8]. (The effective ionic radius increases with coordination number [10]).

Gaebell *et al.* [11] determined the crystal structures of $LiCsCl_2$ and $LiRbCl_2$. For the former, the coordination numbers reported are 5 (tetragonal pyramid) for Li^+ and 9 for Cs^+ in a structure that is isotypic with $CsLuO_2$. For the rubidium salt, Li^+ is tetrahedrally coordinated with F^- and Rb^+ ions are within a bicapped trigonal prism, for which the coordination may be 7, by comparison with the related $SrZnO_2$ structure. It was also shown [12] that $LiCsBr_2$ and $LiRbBr_2$ are isotypic with the corresponding chlorides. Again, for the former, the coordination numbers reported are 5 and 9 for the smaller and larger cations respectively. These workers also report a structure for $Cs_2Li_3I_5$ [13]: Li^+ is coordinated tetrahedrally (2/3) and octahedrally (1/3) with I^- and Cs^+ is accommodated within bicapped trigonal prisms (CsI_8).

The structural evidence for these double salts indicates (not unexpectedly) that the smaller ion is accommodated within sites of lower coordination numbers (4 or 5). The relatively much larger (alternative) cations (CVR values: Li^+/Cs^+–0.0943 and Li^+/Rb^+ 0.125) are in less symmetrical sites, representing higher coordination numbers, 7, 8 or 9. T_m magnitudes for the double salts were invariably considerably less (by 210 to 450 K) than those of their pure constituents and Slopes *F* for these mixtures included many of the largest measured from any of the binary phase diagrams in [3].

One possible explanation for solid compound, double salt, formation is that the combination of cations of disparate sizes permits increased packing efficiency. It appeared reasonable to suppose that the smaller ions might be intercalated to fill partially (at least) some of the unoccupied space within the larger cation alkali halide structures. Accordingly, unit cell volumes for the pure alkali halides were calculated from unit cell edges given by Wyckoff [14] and the 'degree of occupancy' calculated from listed ionic radii [10], assuming 6:6 coordination for these salts (this introduces some error for CsBr and CsI). Comparisons showed that the spherical ions in CsX (6:6 coordination) and in RbX apparently occupied 52–54 and 57.5–60% of the unit cell, respectively. These volumes are ×4–6 the free spaces found in the more densely packed lithium halides, for which occupancy was estimated to be higher, 72–86%. Table 4 shows that the volumes of unit cells for the double halides [9, 11–13] are always closely similar to the sum of the unit cell volumes of the same quantities of the pure constituents. All these volume differences are small (4% or less) and occur in both directions. In most of the double salts, the space occupied by the ions was close to 65% of the unit cell volume. Clearly this is not accommodation of the smaller cation in spaces within the larger structure by increasing the packing density or 'efficiency'.

Comment

The solid double salts, e.g., $LiCsX_2$ and $LiRbX_2$, formed on crystallization of Li/Cs or Rb/X mixtures, demonstrate the significant stability of varied packing arrangements, within which cations of disparate sizes (CVR values are 0.0943 and 0.125) adopt alternative but appropriate coordination dispositions with the common anion. These are quite different from the lattices of the pure salts. For these cation combinations, structures are sufficiently stable to exist in the crystalline state [3], though with T_m values which are significantly below those of the pure components. According to the set/liq model [1, 2], melting occurs when the fusion enthalpy is capable of promoting equilibration involving all suitable alternative, relatively stable, ionic packing arrangements that can participate as regliq zones. It was suggested [1] that the restriction, that only a single crystal lattice can exist in the solid, is relaxed above the T_m. The low T_m values for these double salts may, therefore, be ascribed to the comparatively low stabilities, relative to the liquid

Table 4 Unit cell volumes for crystalline double alkali halides compared with sum of volumes occupied by unit cells for the same amounts of pure salt (nm^3)

Phase	fluoride	chloride	bromide	iodide	
$LiRbX_2$	0.2547	0.4286	0.5051	–	
LiX+RbX	0.2447	0.4197	0.4886	–	
$LiCsX_2$	0.2861	0.4606	0.5346	0.7789	($Li_3Cs_2I_5$)
LiX+CsX	0.2822	0.4807	0.5586	0.7896	3LiI+2CsI

mixtures, of the solid crystals. This may be ascribed to combinations of ions which are capable of forming, in the melt, relatively stable regular, double-salt type, structures (regliq zones) that are different from, and in addition to, those present in the single salt melts [1]. Fusion occurs more readily, at a lower T_m, because the dynamic equilibria of the melt here is stabilized through the participation of all the possible alternative packing arrangements (i.e., those based on structures derived from both the single and all the possible double salt(s) structures). This enhances the stability of the equilibria involving the double salt regliq components in the liquid down to temperatures that are significantly below those characteristic of the fused pure constituent salts, because extra regliq zones are present and contribute to the overall equilibria within the mixture. This presence of additional double-salt regliq components in the melt mixtures accounts for the maintenance of the liquid state below the T_m of their constituents to the, often relatively low, eutectic temperature. This is also consistent with the low T_m values of the double salts.

This model also accounts for the relatively greater values of Slopes I and F for those mixtures that are characterized by greatest size disparities of the varied ionic components, Table 3 and 'Common anion binary mixtures' and 'Common cation binary mixtures'. In the present set of mixtures only the cation combinations Li/Cs or Rb/X form structures that are sufficiently stable to separate as crystalline solids. Nevertheless, in melts formed by the other eutectic-forming mixtures (e.g., Li/K, Na/Cs, Na/Rb, etc. halides, Table 1), comparable regular packing arrangements (binary salt type structures) may be present as regliq zones participating in the liquid equilibria. Because these are relatively less stable, binary salt crystals are not formed but, when such melt mixtures are cooled, a pure (single) component progressively separates, through displacement of equilibria involving the relatively labile double salt regliq species participating. Later the eutectic is formed.

The cooling of mixtures containing varied ions of more nearly comparable sizes results in crystallization of solid solutions adopting (usually) 6:6 coordination, in which the components have not segregated. This is ascribed to the absence of the alternative regliq zones with sufficiently stable packing arrangements in these mixtures composed of ions of more comparable sizes. Only the single most stable lattice structure is adopted, as in the crystallization of the pure salts. The melting points of solid solutions are characterized by relatively small reductions below the T_m values of the components. Behaviour is more closely comparable with that of a single solid and contributions from double-salt type regliq zones to liquid stability are less significant.

Discussion

The principal objective of this comparative survey of fusion of mixtures was to identify the factors that control melting, by formulating a useful representational theory. The analysis was also directed towards obtaining evidence to test the validity and applicability to binary systems of the concepts of the set/liq model proposed in [1, 2]. For this purpose, the careful appraisal of phase diagrams for the melting of binary alkali halide, common ion mixtures, presented in [3] was identified as the most reliable data source available for such comparisons. This critical survey was based on an extended literature appraisal (332 references) within which the inevitable limitations and inconsistencies recognized in the literature data are punctiliously documented and discussed. The systems examined from [3] extended to common ion binary systems those salts that were individually discussed in [1]. These are regarded as the simplest physical and chemical mixtures that are available for this comparative investigation of melting within which the dominant interactions between the spherical ions are strong, but undirectional, electrostatic forces. In [1] the interactions concerned the energetics of packing arrangements involving two ions only: the present extension to the data of [3] (regliq zones) considers some consequences of the participation of structural interrelationships that involve three ions. This comparative analysis extends across a considerable range of relative ionic volume variations, maximum CVR–0.0943 and maximum AVR–0.221, with an overall disparity of ionic volumes to a maximum of Li^+/I^-–0.0412. As discussed below, the pattern of behaviour characterized provides support for, and extends, the set/liq melting model in [1] to contribute towards the development of a comprehensive theory of fusion.

An important unifying feature of this comparative analysis is the consistent general similarity of phase diagram shapes for the 70 binary, common ion, alkali halide mixtures in [3], including the comparable forms of both common cation and common anion sets. While recognizing the inevitability of minor variations of properties, three groups of phase diagrams can be distinguished, as follows.

Compound formation: 8 (perhaps 7) from 13 Systems in group A

For the $LiCsX_2$ and $LiRbX_2$ phase diagrams, eutectic minima are modified by the plateau resulting from the slightly higher T_m values when double salts are formed. Slope I magnitudes were amongst the largest measured here, 3.5 to 5.4 K, with subsequent, also large, increases of Slope F values to about 8.0 to 14.5 K.

Eutectic formation: groups A, B and E (38 mixtures)

Mixtures of all three groups (A, B and E) formed well-defined eutectics. Those of group A, all containing the smallest of the ions considered, Li+, were characterized by relatively large values of Slopes *I* and *F*. For mixtures in groups B and E, these slopes were somewhat less: the relatively smaller constituent ions, Na+ and F− are appreciably larger than Li+. It is concluded that the shapes (i.e., Slopes *I* and *F*) of these phase diagrams are determined mainly by the (relative) size of the smallest component.

Solid solution formation: groups C, D, F, G and H (32 mixtures)

When the AVR or CVR values were about 0.4 to 0.5, many phase diagrams were approximately symmetrical. Some exhibited transitional behaviour, solid solutions (e.g., Na/K/Cl, Br or I) initially formed on cooling subsequently recrystallized at lower temperatures to separate into the component phases. As AVR or CVR values increased above 0.55, and towards unity, the maximum diminutions of liquid temperatures of the melts, below T_m values for the components, became smaller, values of Slope *I* progressively diminished and Slope *F* was no longer significant. There was also a tendency for phase diagrams to become asymmetric, Slope *I* magnitudes were (usually, but not invariably) relatively larger when the salt containing the larger varied ion was added to that containing the smaller.

Melt structure, Set/liq model

The set/liq model for melting is described in Part 1 and is discussed throughout [1, 2]. Comparative considerations of enthalpy and density changes on alkali halide fusions were consistent with the formation of the following pattern of participating ionic coordination structures in the melts close to the T_m. The preferred structure in molten lithium halides was identified as 4:4 coordination, though the presence of the 6:6 form was indicated for LiI. It was inferred that there are approximately equal proportions of the 4:4 and 6:6 forms in the liquid sodium halides. Similar regliq structures were indicated for the fused potassium halides but with a higher proportion (around 70%) of the 6:6 component, possibly together with some of the 8:8 form. Melts of the rubidium and caesium halides were believed to contain increasing proportions of structures with the higher coordinations, 6:6 and 8:8. Overall, it was concluded (in accordance with expectation) that the proportions of the more highly coordinated forms increased with cation size (Li to Cs) and, perhaps to a slightly lesser extent, with

anionic size (F to I). The influences in controlling the structures present in the liquid appeared to be greatest for the smallest ion, Li+, but also with significant effects by Na+ and F−.

Set/liq melting model and eutectic formation

The (often curved) lines, between T_m values for the component salts and the eutectic point, on the phase diagrams in [3], define the lowest temperature at which a mixed melt of that composition can exist. In such mixtures, at temperatures immediately below the T_m of Salt A, added Salt B can be regarded as 'dissolved' in liquid Salt A. During progressive cooling, the composition range across which the mixture can remain molten progressively diminishes through the deposition of Salt A. Ultimately, at the eutectic, the remaining liquid solidifies with separation of the components to form a mixture of the individual crystal phases (Salt A +Salt B). Eutectics are formed only by those salt combinations for which the total lattice potential energy difference is sufficient to separate the components on cooling (about 65 kJ mol^{-1} or more, Tables 1 and 2, 'Comment'). These systems include those mixtures that also form crystalline double salts (Table 4). At lower energy differences, for mixtures containing varied ions of more comparable sizes, melts crystallize as solid solutions, composed of random distributions of ions in an unseparated 'common phase'.

Eutectics were formed from mixtures of ions having the greatest size disparities, here including the smallest ions. The eutectic phase diagrams, characterized by largest Slopes *I* and *F* (Table 3), were found for the mixtures of Group A, all of which included the smallest ion, Li+. A similar trend, though with somewhat smaller slope values, was characteristic of Groups B and E in which one or more of the smallest ions (Li+, Na+, F−) was invariably present. Those mixtures for which the AVR and CVR values were about 0.6, and above, formed solid solutions. The mixtures of Groups C and E showed intermediate behaviour in which characteristics of both E and SS formation could be recognized. No correlation was found between the differences (or ratios) of calculated U_{POT} values for the binary mixture components and the trends of Slopes *I* or *F* values.

The Slopes *I* (and also Slopes *F*) for the two sides of the phase diagram for eutectic forming mixtures (also double salts) often have comparable magnitudes. Columns 4 and 7 in Table 3 express the approximately symmetrical features of these mixtures from [3]. Thus, the (molar) influence of added Salt B in lowering the T_m of Salt A is comparable with the ability of Salt A to diminish the T_m of Salt B. This symmetry can be ascribed, on the set/liq model, to the formation of a 1:1

double salt, AB, which contributes additional regliq structures to the dynamic equilibrium, stabilizing the liquid phase below the T_m of one (or both) components. The equimolar composition accounts for the comparable behaviour of the melt on both sides of the phase diagram. Moreover, six of the seven mixtures mentioned in Table 4 have the 1:1 composition ratio and form structures that are sufficiently stable to give crystalline solids with low T_m values. On the set/liq model this is ascribed to the presence in the melt of regliq structures based on regular three ion packing arrangements (double salts) that are stable in the liquid at temperatures below the T_m values of the constituent salts. Equilibria in these mixtures involve all regliq structures that involve each and every component, including every possible double salt structure of sufficient stability to participate. All such double salts, existing in a dynamic fluid structures may not, however, be capable of crystallization as solids. The involvement of additional and different structures (from those that form crystals) in the energy-enhanced equilibria that characterizes the melt has been discussed for single salts in [1]. This representation accounts for two aspects of the above observations for the alkali halides. The low T_m values for the known double salts are ascribed to the low temperature stability of equilibria involving all possible regliq structures. The dominant participation of 1:1 double salts in the systems considered here, Table 4, explains the symmetry of many of the phase diagrams in [3].

The sequence of changes during cooling of a representative binary alkali halide melt, consisting predominantly of Salt A, but containing a small proportion of Salt B, may be portrayed as follows. Immediately below the Salt A T_m, a majority of the liquid is composed of the regliq zones characteristic of Salt A (based on stable 4:4, 6:6 and/or 8:8 coordinations of the two ions [1]). Small amounts of those regliq zones that are characteristic of the pure Salt B melt may also be present. However, the AB combination introduces, into the dynamic equilibrium of the liquid, additional regliq structures, derived from the double salts, which stabilize the liquid at temperatures below the T_m of Salt A. These zones include all possible (and sufficiently stable) regular lattice arrangements for the packing of three ions present in the AB melt, together with all other similarly stable structures based on other composition ratios, A_xB_y. The presence of phases other than those of 1:1 ratio accounts for asymmetry in the magnitudes of Slopes *I* and *F*. On cooling the mixture considered, the single (almost) pure Salt A separates and the proportion of Salt B present in the double salt regliq components increases. This rise in the contribution from the participating AB, and any other, structures progressively stabilizes dynamic equilibria in the remaining liquid, within a diminishing composition range as the temperature is reduced. Eventually, either a stable double salt is crystallized (as from Li/Cs or Rb/X) or, for the other mixtures where no crystalline binary salt is known, the components of the dynamic equilibrium separate to give the Salt A+Salt B eutectic. The participation of labile double compounds, present as local and regular arrays (regliq zones), in those mixtures which do not give a crystalline double salt on solidification, accounts for the existence of the stable liquid phase at temperatures below the T_m values of the constituents. Facile dissociation to form the more stable single solids means that the small zones of regliq structures contributing to the melts do not appear as crystals that separate when the promoting effect of ΔH_F on the dynamic equilibria is relinquished at T_m. The presence of alternative possible packing arrangements for ions from both the individual components and the double salt structures in the liquid accounts for the instances of eutectic formation listed in Tables 1 and 2.

The following properties of alkali halide melt mixtures explain their ability to remain liquid at temperatures below the T_m values of their constituents.

Regliq domains: different structures present

Small regliq zones, each of a regular ionic structure as envisaged for pure alkali halide melts [1], are expected to be present for both individual salts in mixtures and to participate in the dynamic melt equilibria [1]. The diversity of structures at high temperatures (in melts) is suggested because alkali halide structures do not all conform with crystallographic expectations for 'sphere packing' [1, 15]. It can, therefore, be anticipated that, with an appreciable contribution of energy to the system ($+\Delta H_F$ above T_m), various alternative, stable and regular structures similar to those that are present in crystalline solids can contribute to the participating domains in the melt. The mixtures considered here contain three ions [3] and are, therefore, regarded as increasing the number of possible regliq structures that contribute to the dynamic melt equilibria. For example, for the mixture (LiF+CsF), in the regliq zones representing the individual components, Li in the LiF component is expected [1] to be largely, if not exclusively, incorporated in 4:4 (F^-) coordination sites. Similarly, the caesium, in the CsF contribution, is expected [1] to be located mainly in arrays of higher coordinations, 8:8 and 6:6. However, in a mixture, there is the additional possibility of double salt formation wherein there are at least two forms of coordination [9] (and perhaps other variant arrays) to accommodate the two cationic components (4 or 5 for Li, 7, 8 or 9 for Cs, 'Double salt formation: $LiCsX_2$ and $LiRbX_2$'). Structures, other than those known from the double salt crystals

of these low T_m solids, may contribute to the stability of the melt by participating in the dynamic equlibria.

Eutectic temperature diminution, ΔT_X

(ΔT_X is defined as the difference between the eutectic temperature and that of the point corresponding to the eutectic composition on the straight line joining the T_m values of Salt A and of Salt B on the phase diagram. ΔT_X is the composition-weighed mean of the T_m reduction for eutectic formation.) With the exception of the Li/Cs, Rb and K/X mixtures (discussed in 'Regliq domains: double salts' below), all ΔT_X values estimated from the data in [3] for those binary, common ion mixtures that form eutectics were between 145 and 225 K. It is concluded that values of ΔT_X greater than 140 K are identified with the formation of a eutectic whereas solid solutions are formed when ΔT_X is less than 130 K.

Regliq domains: double salts

Comparative examination of those phase diagrams [3] that include double salt formation, $LiCsX_2$ and $LiRbX_2$, show that ΔT_X values, estimated by linear extrapolation of the Slopes F, are between 305 and 390 K. However, these lowest temperatures are never achieved by the melt because (and only for these mixtures, Tables 1 and 2) crystalline double salts are formed which melt about 60 K (values were between 40–100 K) above each estimated eutectic T_m. ΔT_X values for the Li/K/X mixtures are within a slightly lower range, 260 to 360 K, but, for these, the formation of a crystalline double salt was not detected [3]. This may be due to the high T_m values for the potassium halides, which are all appreciably greater (by more than 30 K) than those of the corresponding rubidium and caesium halides. Thus, formation of a crystalline double salt is not possible in Li/K/X mixtures because the components separate as the individual solid alkali halides, to form eutectics, at somewhat higher temperatures. Nevertheless, regular two-component structures representing these double salts may be present as regliq zones participating in melt equilibria. This accounts for the relatively large ΔT_X values that characterize the Li/K/X mixtures. Double salts do not crystallize on cooling of the several other mixtures that form eutectics, Tables 1 and 2, but regular structures of constituents containing three ions (double salts) may participate as regliq components in the energy-enhanced dynamic melt equilibria [1, 2].

Irregliq: connective material

The maintenance of dynamic equilibria between small domains of alternative, regular structures in the melt requires the presence of connective interphase material that forms the contact interfaces between the more perfect (regliq) zones [1, 2]. Inevitably, such connective material must be imperfect, the interfacial ions being (temporarily) disposed at sites that represent stability compromises between adjoining regular arrays. Formation of these defective regions, analogous to grain-boundaries in solids, (presumably) requires a contribution from ΔH_F. However, for mixtures containing ions of three different sizes, strain within imperfect interface material will be minimized by appropriate packing. Thus, because melting involves the proliferation of disordered zones that permeate the material, fusion is facilitated by increasing the diversity of ionic sizes present in these mixtures.

Ionic size

From comparisons of the Slopes I and F, Table 3, it is concluded that the greatest determining influence in eutectic formation and, indeed generally in diminishing T_m values of mixtures, is the participation of ions of disparate sizes. The trends observed are most obvious for the smallest ion, Li^+, but are also significant for Na^+ and F^- and may result from differences in lattice energies, ionic polarization effects, etc.: high values of these properties are associated with small ions. Furthermore, their small sizes may permit their greater diffusive mobility amongst and between their larger neighbours, particularly in the irregliq material. This ability is expected to be largest for Li^+ and appreciable, but less, for Na^+ and F^- (Table 3). It is also noted that the T_m values for LiCl, LiBr and LiI are the lowest of all the alkali halides and T_m for LiF is below the values of NaF and KF (Fig. 1 of [1]). Overall, the presence of relatively small ions appears to facilitate melting. Mixtures composed of ions of more nearly comparable sizes tend to form solid solutions, or a compromise crystal structure, when AVR or CVR ratios are greater than 0.6, Tables 1 and 2.

Solid solution formation

Solid solutions are formed on cooling mixtures with AVR or CVR values greater than 0.6 and for which the difference in lattice potential energies is below about 65 kJ mol^{-1}, Tables 1 and 2. Furthermore, T_m differences for pairs of salts that form solid solutions are, in general, relatively small, less than 100 K. (T_m differences were usually, but not invariably, greater for those salt combinations that formed eutectics.) The distinction between SS and E formation is not always complete, examples of intermediate behaviour have been mentioned above. Mixtures composed of cations or anions having approximately comparable sizes undergo solid solution formation that is akin to

single salt crystallization. While the fluid state of the mixture may be maintained below the T_m of at least one component, only a relatively limited temperature diminution occurs before solidification. This considerable tendency to crystallize, particularly below the lower T_m of the two constituents, accounts for the asymmetry of those phase diagrams, mentioned in 'Group G' and 'Group H'.

Eutectic compositions and T_m values of the component salts

A composite plot of eutectic compositions, for the binary mixtures from [3], *vs.* T_m differences for the pure components, is shown in Fig. 2. For eutectic-forming systems, the phase diagrams tend to be symmetrical and the overall average Slope *I* is 3.75±0.60 K ('Notes for Table 3'). As expected, and as confirmed by Fig. 2, eutectic compositions depend on the T_m differences of the component salts. The greater this temperature difference, the smaller is the proportion of the higher T_m component in the eutectic mixture, Fig. 2. The scatter of data points arises because of the relatively large influence by the smaller ions and the experimental uncertainty. (Most T_m differences for the solid solution forming mixtures were below 100 K and no trend of variation with composition was found.)

Eutectic melting temperatures and eutectic compositions

T_m differences (Salt A – binary eutectic/K) and the proportion of Salt A in that eutectic are shown for the
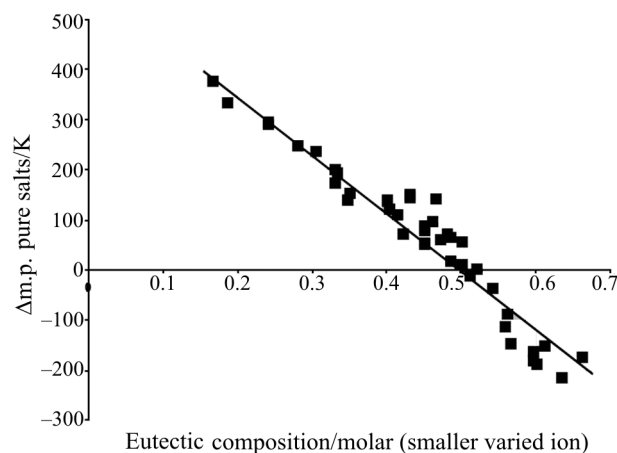
common anion and for the common cation mixtures in Figs 3 and 4, respectively. Two points were obtained from each phase diagram in [3].

Common anion mixtures

In Fig. 3, common anion mixtures, the lower line represents all the lithium-containing mixtures (probably more satisfactorily represented as a slight curve, concave downwards). The upper line is close to the points for the comparable sodium-containing mixtures. The trends for the other (larger) cations were less evident. This is consistent with the patterns of behaviour discussed above.
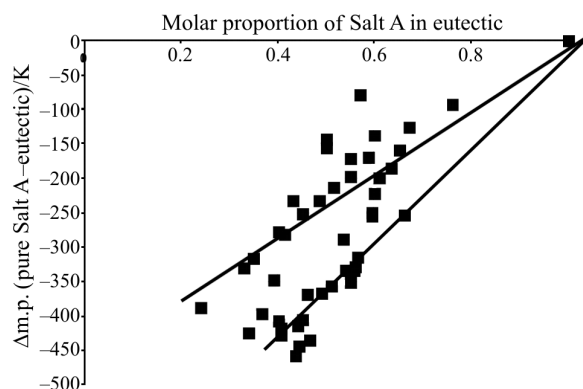

Fig. 3 Binary alkali halide, common anion mixtures that form eutectics [3]: plot of the differences (T_m of Salt A – eutectic/K) and the molar proportion of Salt A in each eutectic (two points from each phase diagram [3]). The lower line represents mixtures containing Li/K, Rb or Cs: the upper line is close to the points representing the comparable Na containing mixtures
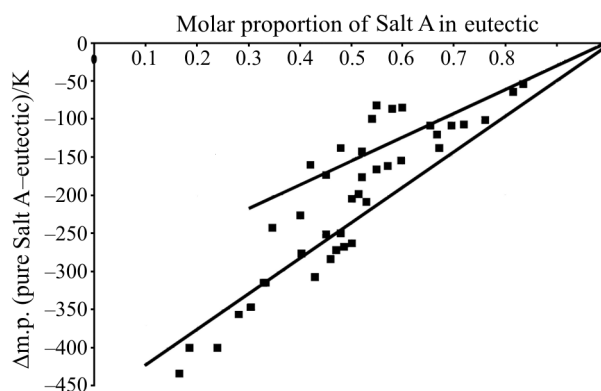

Fig. 2 Plot of T_m (K) differences for components of binary alkali halide mixtures (smaller varied cation/anion – larger) *vs.* eutectic compositions (molar proportion of the smaller alternative ion): data for all eutectic-forming mixtures from [3]. The line passes through the temperature difference zero for the equimolar eutectic

Fig. 4 Binary alkali halide, common cation mixtures that form eutectics [3]: plot of the difference (T_m of Salt A – eutectic/K) and the molar proportion of Salt A in each eutectic (two points from each phase diagram [3]). The lower line represents all the fluoride-containing combinations (F/Cl, Br or I) and the upper line is close to the more widely scattered values for the Cl/I eutectics

Common cation mixtures

In Fig. 4, the lower line (again probably more accurately represented as a slight curve, concave downwards) is close to all points for fluoride-containing mixtures: F/Cl, Br or I with all five cations. The upper line is close to all data for the Cl/I mixtures. The other systems, Br/Cl or I did not form eutectics. This is consistent with the trends discussed above: the larger the value of Slope *I* the smaller proportion of that component in the eutectic.

Eutectic temperature and melting points of component salts

Differences between the T_m of the less fusible component of the binary mixture and the eutectic (/K) are plotted against CVR and AVR in Figs 5 and 6, respectively. For both sets, the magnitude of the 'eutectic T_m diminution' rises considerably with increase in disparity of sizes of the varied cation or anion. For the common anion mixtures, Fig. 5, the largest number of data points were available for the lithium containing mixtures, where there was a linear, though scattered, trend. Values for the other cations were comparable but no distinctive trends were identified. For the common cation mixtures, Fig. 6, the T_m temperature differences were relatively largest for the lithium containing mixtures, slightly less when sodium was present and data for the other three cations were comparable, though somewhat smaller.
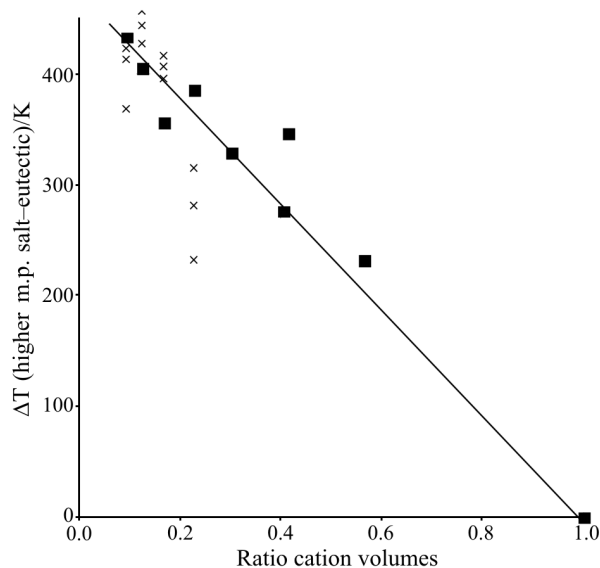
It is concluded, from the distributions of points on Figs 5 and 6, that the disparity in sizes of the varied ions in the mixtures is a dominant reason for the relatively low T_m values of the eutectics. The influence of the common ion is most significant for the smallest ions, Li^+ and Na^+. A possible explanation is that the relative ease of small cation movements, between the significantly larger anions present, contributes to and maintains disorder by inhibiting the development of the long-range order that is characteristic of a crystalline solid. This effect is less in mixtures containing ions of more comparable sizes.

Eutectic composition and ionic size

For common cation mixtures the molar proportion of Salt A (smaller anion) in the eutectic increased in di-
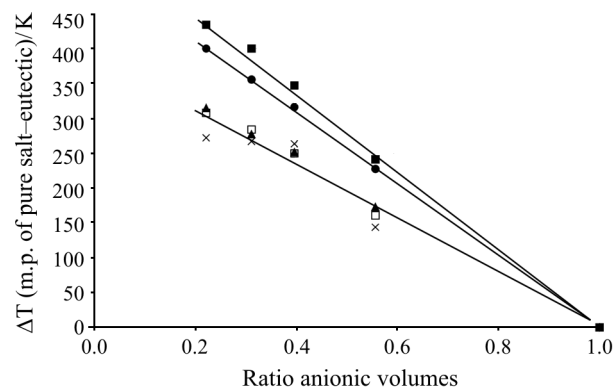
Fig. 6 Binary alkali halide, common cation mixtures that form eutectics [3]: plot of (higher T_m pure salt–eutectic temperature)/K vs. AVR: ■ – Li^+, ● – Na^+, ▲ – K^+, □ – Rb^+, × – Cs^+; lines have been extrapolated to the intercept at (1, 0) representing the pure salt

Fig. 5 Binary alkali halide, common anion mixtures that form eutectics [3]: plot of (higher T_m pure salt – eutectic temperature)/K vs. CVR. Mixtures containing fluoride as the ■ – common ion, × – all other common anions. The line has been extrapolated to the intercept at (1, 0), representing the pure salt
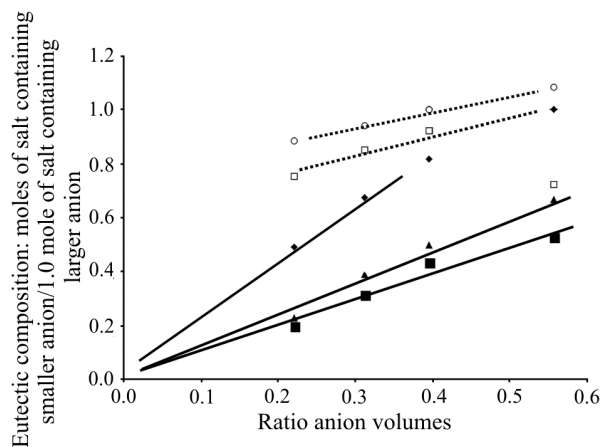
Fig. 7 Binary alkali halide, common ion mixtures that form eutectics [3]: plots of eutectic composition molar ratios (smaller cation/larger cation) vs. AVR. Full lines, in order of increasing slopes, refer to ■ – Li, ▲ – Na, ◆ – K; the interrupted lines are the mixtures containing □ – Rb and ○ – Cs

rect proportion to the AVR of the constituent salts: full lines in Fig. 7 for Li, Na and K. Different trends were found for the mixtures containing Rb and Cs: dotted lines in Fig. 7. A similar analysis for the common anion sets (figure omitted here) showed much greater scatter of data, except for the mixtures containing fluoride where there was a direct proportionality, very similar to that shown for sodium on Fig. 7. These (approximately linear) relationships between eutectic composition and ionic component sizes are (again) most significant for the smallest ions present.

Conclusions

In Part 1 [1] it was demonstrated that the energy and density changes that accompany alkali halide melting are relatively small. The structural disorder introduced by fusion must be limited in extent. These changes can be represented by the generation in the liquid of rapid, dynamic rearrangements of ions between small domains composed of the alternative possible, locally regular, crystal-type and relatively stable structures. The set/liq model is based on the assumption that ionic dispositions in the melt, above the T_m, are controlled by the same strong, but undirectional, electrostatic forces of attraction and repulsion responsible for crystal cohesion. Interconversions between the different but relatively stable regliq structures participating in the liquid equilibrium are made possible and sustained by the enthalpy of melting. This multiplicity of structural forms is ascribed to the incorporation of the additional energy (ΔH_F) which, in the liquid, relaxes the restriction applicable to crystalline solids, that only the single and most stable lattice structure can be present. Each regliq zone, consisting of one of the alternative possible regular structures, is small so that long-range order is not evident or maintained: there is little beam reinforcement in X-ray diffraction. Constant, rapid movements of ions sustain this three-dimensional coherent assemblage, with all contributing regliq zones in dynamic equilibrium, across the intervening, less structurally regular, contact interfaces of irregliq material. The mobility of the ions that participate in the transfer of material at the irregliq interfaces, permeating the liquid phase, confers the fluid properties on the bulk melt.

The present article offers an analysis that extends the set/liq model [1, 2] to a consideration of the melting of mixtures, by comparative examination of the wealth of reliable information on binary, common ion, alkali halide phase diagrams provided by Sangster and Pelton [3]. The feature of interest, for the theory of melting, is the ability of these salt mixtures to remain liquid below

the T_m values of the components. On the set/liq model [1], this can be ascribed to stabilization of the melt mixtures through contributions to the overall equilibria from the additional regliq domains that represent all possible alternative structures of the double salts present in these binary mixtures.

Ionic structures in mixed melts

Regliq zones, the components of the melt that are regarded as including all possible stable variants of ordered ionic packing, including also three-ion (double-salt type) arrays, from the A/B/X or A/X/Y mixtures. This extension of diversity of participant structures in the mixed melt equilibria is expected to stabilize the liquid phase to lower temperatures, so that the regliq compositions are qualitatively and quantitatively different from those characteristic of the individual pure component molten salts [1].

Regliq zones, representing various stoichiometric compositional ratios (possibilities may include: ABX_2, AB_2X_3, etc., or A_2XY, A_3X_2Y, etc.), are the alternative stable structures of the double salts in the mixtures. These are suggested as potential contributors to the equilibria and thereby enhance stability of the liquid phase. As with the pure salts [1], there may regular ionic structures in the molten mixtures that participate in the dynamic system represented by the relatively energy-enhanced melt ($+\Delta H_F$) but that are not sufficiently stable to separate as a crystalline double salt phase on cooling. It is considered significant that the crystalline double salts that are formed from the mixtures Li/Cs or Rb/X (Table 4) melt at much lower temperatures than the T_m values of the pure constituents. It appears, therefore, that equilibria involving structures characteristic of 'double salt' combinations may be stable as liquids to relatively low temperatures and 'single salt' components [1] probably also participate. Thus, T_X values are greatest for those mixtures that have been shown [3] to form double salts (apparently the most stable) and those for the Li/K/X mixtures may be only slightly less. T_X values for the other eutectic-forming mixtures are appreciably smaller, attributable to lower stabilities, and, therefore, smaller participating amounts of the 'double salt' structures contribute to the dynamic regliq melt equilibria. When T_X is below 130 K, it appears that the role of 'crystal-type binary compound' regliq zone formation is less significant in stabilizing the liquid to low temperatures. The more closely comparable sizes of the varied ion in these mixtures allow a compromise common lattice spacings to be adopted, which results in crystallization of a single phase solid solution.

The apparent preference of the 1:1 cation ratio for double salt formation in most of the Li/Cs or Rb/X mixtures (Table 4) suggests that structures based on

this stoichiometric composition may be the most stable. This is entirely consistent with the overall symmetry, characteristic of many of the phase diagrams in [3], which is, therefore, ascribed to a tendency towards (approximate) equality of interactions by both of the varied ions present in these mixtures. Some further behaviour patterns within the sets of phase diagrams, specifically ascribing relatively greater control of melting properties to the smallest ions in these mixtures (Li^+, Na^+, F^-), have been observed, Figs 2–7. These are entirely consistent with the principles proposed for the set/liq model melt structure which, therefore, is regarded as providing a potentially useful representation of these ionic liquids. Part 3 [16] will extend discussion of the concepts described here towards presenting the melting process in a more general perspective.

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