The Solution of Alkaline Earth Metals in Their Molten Halides. III. The Densities of Melts in the Systems Barium — Barium Chloride, Barium — Barium Bromide and Strontium — Strontium Chloride

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The densities of melts in the systems $Ba-BaCl_2$, $Ba-BaBr_2$
and $Sr-SrCl_2$ for concentrations up to about 7 mol % metal have been
measured by the buoyancy method. The densities were found to
decrease less rapidly with concentration than expected for a model
where the alkaline earth metal dissolves upon forming the monovalent
Me^+-ion. For comparison, the densities of two melts in the system
$CsCl-BaCl_2$ and one melt in the system $RbCl-BaCl_2$ have also been
measured.

The magnetic susceptibility of solutions of barium metal in molten barium
chloride and barium bromide as well as strontium in strontium chloride has
been measured.[1,2] The results shed light on the nature of these solutions, but
many questions remain unanswered, and it is still not possible to present any
detailed picture of the structure of these liquids.

Some authors have considered a model for these liquids in which each
alkaline earth metal atom, Me, dissolves upon forming two monovalent ions,
according to the scheme:

$$Me+Me^{2+} \rightarrow 2\ Me^+ \tag{1}$$

Correspondingly, our magnetic susceptibility measurements [1,2] have detected
the presence of a paramagnetic component in the mixtures (though somewhat
less than predicted by a complete conversion according to the above reaction
scheme). The above dissolution scheme is equivalent to assuming the solution

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to be a mixture of a monovalent alkaline earth halide with a divalent alkaline earth halide ($MeX - MeX_2$). Hence, if the dissolution took place according to the above scheme, the volume change of MeX_2 by adding Me would presumably depend mainly on the size of the monovalent Me^+ ion formed, and less on its nature. Thus the volume behaviour could be reproduced by substituting the monovalent alkaline earth ion by another monovalent cation of the same size. It is therefore possible to investigate if the volume behaviour would be reproduced by using any of the alkali halides as a source of monovalent cations.

In the following, we report some density measurements which enable us to compare the volume behaviour on adding an alkaline earth metal to a halide melt of the same metal, with the volume behaviour of adding an alkali halide to the alkaline earth halide melt.

EXPERIMENTAL

Chemicals. The origin (or preparation) and handling of barium, barium bromide, barium chloride, strontium and strontium chloride have been described elsewhere.[1,2] Rubidium chloride and caesium chloride, Merck *p.a.*, were dried in vacuum at about 200°C for 20 h prior to use.

Procedure. The densities were measured by the buoyancy method. The apparatus consisted of a recording thermovacuum balance, which also permitted the use of a controlled atmosphere. The apparatus has been described by Lillebuen.[3] High purity argon gas from Norsk Hydro was used as atmosphere in the $Ba - BaX_2$ and $Sr - SrCl_2$ systems. A similar quality nitrogen gas was used with the $AlkX - BaX_2$ experiments. The air in the apparatus was replaced by repeated evacuations and flushings. The inert gas was also slowly flushed through the apparatus during the experiment. The crucibles and the sinkers were made of molybdenum for the alkaline earth metal – metal halide systems and platinum-10 % rhodium for the $AlkX - BaX_2$ systems. The volumes of the sinkers were about 1.30 cm³ and 1.94 cm³, respectively. These volumes were accurately calibrated with distilled water at room temperature. They were employed for obtaining the high temperature volumes, using published values for the linear thermal expansion coefficient of molybdenum[4] and of platinum-10 % rhodium.[5]

The sinker could be moved vertically on the sample container and this was used to facilitate mixing. (It was observed that the mixing process was rapid in the $Ba - BaX_2$ systems, whereas the equilibrium was reached more slowly in the $MCl - BaCl_2$-systems). Corrections for the effect of the surface tension on the sinker suspension were also made.[3] Measurements were undertaken at several different temperatures for each composition.

The observed densities were reproducible with a standard deviation of about 0.002 g/cm³. Due to systematic errors, such as impurities in the chemicals, the absolute values of the densities are perhaps slightly less accurate than indicated above. The estimate of the error will be valid for the *changes* in density with composition within the same binary system, however.

RESULTS AND DISCUSSION

The experimental densities in g/cm³ obtained at several temperatures for each composition were fitted by a least squares approximative to an equation which was linear in temperature. The coefficients of these equations are given in Tables 1 and 2.

The experimental densities were converted to molar volumes in order to compare the $Me - MeX_2$ systems with the $AlkX - MeX_2$ systems (Me, Alk, and X being the alkaline earth, alkali, and halide, respectively). The molar volume, V_m, of mixtures in the $Me - MeX_2$ systems is defined as the volume

Table 1. Observed densities in g/cm³ for mixtures in the systems $Ba-BaCl_2$, $Ba-BaBr_2$ and $Sr-SrCl_2$, respectively, fitted to the equation $d^t = d^{t_0} - a(t - t_0)$. Here t is the temperature of the observation in degrees centigrade, d^{t_0} is the density at the reference temperature t_0, N_{Na} and N_{Sr} are the "mol" fractions of barium metal, and strontium metal, respectively.

N_{Ba}	N_{BaCl_2}	Density at 1000°C	$a \times 10^4$ $t_0 = 1000°C$	Temperature range of measurements °C
0.0000	1.0000	3.134	6.7	986 − 1036
0.0218	0.9782	3.136	6.0	976 − 1027
0.0318	0.9682	3.135	6.9	998 − 1023
0.0494	0.9506	3.132	6.5	983 − 1033
0.0728	0.9272	3.132	6.1	985 − 1026

N_{Ba}	N_{BaBr_2}	Density at 900°C	$a \times 10^4$ $t_0 = 900°C$	
0.0000	1.0000	3.905	9.2	882 − 1005
0.0206	0.9794	3.899	10.3	896 − 988
0.0216	0.9784	3.899	9.0	878 − 968
0.0541	0.9459	3.895	8.8	870 − 979
0.0692	0.9308	3.885	9.2	889 − 999

N_{Sr}	N_{SrCl_2}	Density at 900°C	$a \times 10^4$ $t_0 = 900°C$	
0.0000	1.0000	2.703	5.8	892 − 1013
0.0190	0.9810	2.695	5.6	895 − 1008
0.0352	0.9648	2.690	5.9	904 − 1006
0.0396	0.9604	2.688	5.9	903 − 1008
0.0692	0.9308	2.681	5.8	906 − 1014

Table 2. Observed densities, d^t, for melts in the systems $MeCl-BaCl_2$ (where Me is Cs and Rb) are fitted to an equation $d^t = d^{1000} - a(t - 1000°C)$. Here t is the temperature and d^{1000} is the density in g/cm³ at 1000°C. N_{MeCl} is the "mol" fraction of the chlorides.

N_{RbCl}	N_{CsCl}	N_{BaCl_2}	d^{1000}	$a \times 10^4$	Temperature range of measurements, °C
0.1550	0	0.8450	2.970	6.7	961 − 1015
0	0.0469	0.9531	3.101	7.2	965 − 1018
0	0.1595	0.8405	3.016	7.0	962 − 1016

containing Avogadros's number of Me atoms counted irrespective of oxidation state. In the $AlkX - MeX_2$ systems the molar volume, V_M, refers to the mixture where the sum of Me atoms and Alk atoms equals Avogadro's number. We shall assume that the molar volumes in the latter systems are additive, thus obeying the following equation:

$$V_\mathrm{M} = N V_\mathrm{AlkX} + (1 - N) V_\mathrm{MeX_2} = V_\mathrm{MeX_2} + N(V_\mathrm{AlkX} - V_\mathrm{MeX_2}) \qquad (2)$$

Here N is the mol fraction of the alkali halide and V_AlkX and $V_\mathrm{MeX_2}$ the molar volumes of the pure alkali halide and the alkaline earth halide, respectively. Using our own experimental values for $V_\mathrm{MeX_2}$ together with values for V_AlkX derived from densities collected by Janz [6] we have plotted the curves of V_M versus N according to the above equation. Figs. 1, 2, and 3 show the curves for the barium chloride, barium bromide and strontium chloride systems, respectively.
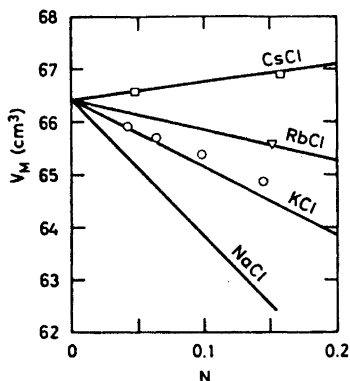

Fig. 1. Molar volumes, V_M, at 1000°C of mixtures in the systems AlkCl − BaCl$_2$ versus the mol fraction, N, of alkali chloride. Fully drawn lines are calculated curves. Point shown as squares are observed for the CsCl − BaCl$_2$ system, the triangle is observed for the RbCl − BaCl$_2$ system, the circles represent observed molar volumes for the Ba − BaCl$_2$ system (N is here defined as N_BaCl or $2N_\mathrm{Ba}$).
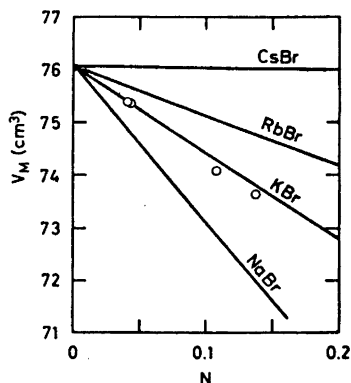
Fig. 2. Molar volumes, V_M, at 900°C of mixtures in the systems AlkBr − BaBr$_2$ versus N, the mol fraction of alkali bromide. Fully drawn lines are calculated curves. Circles represent observed molar volumes in the Ba − BaBr$_2$ system plotted against N (N is here defined as N_BaBr or $2N_\mathrm{Ba}$).

The assumption that excess molar volumes of mixing can be neglected for our purposes has been verified for two barium chloride systems. Fig. 1 shows that the experimental molar volumes (calculated from the densities in Table 2) of two CsCl − BaCl$_2$ mixtures and of an RbCl − BaCl$_2$ mixture lie close to the corresponding calculated curves.

Assuming that each alkaline earth metal atom (Me) on dissolution reacts to form two monovalent alkaline earth ions we have:

$$N_\mathrm{MeX} = 2N_\mathrm{Me} \qquad (3)$$

where N_Me is the "weighed in" mol fraction of alkaline earth metal and N_MeX the mol fraction of the hypothetical alkaline earth monohalide in the mixture. The plot of the experimental molar volumes (derived from the data in Table 1) of the Me − MeX$_2$ mixtures against $N_\mathrm{MeX}(= 2N_\mathrm{Me})$ is shown in Figs. 1 − 3. For the systems containing barium it appears that the observed effect
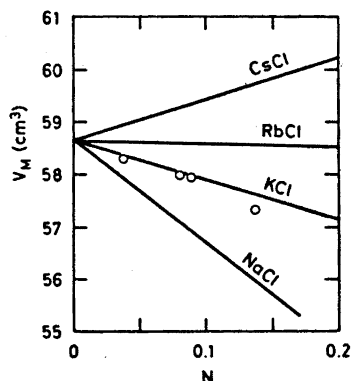
Fig. 3. Calculated molar volumes, V_M, at 900°C of mixtures in the systems AlkCl − SrCl$_2$ *versus* the mol fraction, N, of the alkali chloride (fully drawn lines). Circles represent observed molar volumes in the Sr − SrCl$_2$ system plotted against N (N is here defined as N_{SrCl} or $2N_{Sr}$).

of the barium metal on the mixture is similar to that of the K^+-ion. Comparing the barium − barium chloride system with the strontium − strontium chloride system, it is seen that the former system exhibits volumes slightly above, the latter slightly below that of the systems containing potassium chloride. These results would seem to contradict the hypothesis that the melts contain major amounts of monovalent alkaline earth cations, because the monovalent Sr^+ and Ba^+ ions certainly would be substantially larger than the K^+-ion. According to Pauling [7] the univalent radius of barium is 1.53 Å, as compared with 1.48 Å for Rb^+ and 1.69 Å for Cs^+. The Pauling univalent radius for barium is the radius the Ba^{2+} ion would have, if it was to retain its electron distribution (xenon type), but enter into a Coulomb interaction as if it had a single positive excess charge. The single outer electron of the real Ba^+-ion, however, would occupy a space demanding 6s orbital, rather than be confined within a xenon type electron shell. Hence, it is reasonable to assume that the Ba^+-ion would have an ionic radius larger than the univalent radius given by Pauling. The molar volumes in Figs. 1 and 2 for the Ba − BaX$_2$ systems should therefore have increased rather than decreased with metal addition, if the monovalent cation had been the major species formed by the metal on dissolution.

The potassium ion has an ionic radius (1.33 Å) very similar to that of the divalent barium ion (1.35 Å). This is suggestive of the following ideas about the barium − barium halide liquid.

The dissolved barium metal atom loses its two outer electrons. These two electrons must to a large degree occupy unrelated locations as solvated electrons in the melt. Hence, the equilibrium fraction of Ba^+-ions is small. Assuming that the Ba^{2+}-ions do occupy cation positions in the melt not very different from those of a K^+-ion (*i.e.* that there are no large structural differences between the KX − BaX$_2$ melt and the Ba − BaX$_2$ melt), it follows that the solvated single electron exhibits little or no effect on the volume.

Similar considerations may hold true for the strontium system, although in this case the volume of the system is slightly too large. This could be due to the presence of a somewhat larger, but still small equilibrium fraction of Sr^+-ions or to partial invalidity of the above hypotheses about the volume effects of the different species.

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