Densities and Excess Volumes of Fused Halides

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Densities of molten AgBr-AX (A = Li, Na, K, Rb, Cs; X = Br or Cl), AgBr-AgCl, KBr-NaBr, KBr-CsBr, KCl-KBr, and KCl-CsBr mixtures have been measured at 0.5 mole fraction using the method of Archimedean displacement. The excess volumes of mixing are all positive, except for the AgBr-LiBr system. Attempts to relate the excess volumes of the binary AgBr-ABr systems to the second order conformal solution theory of Reiss, Katz, and Kleppa are unsuccessful, since V^E is large even when the diameter difference parameter, δ_{12}, is close to zero. However, the excess volumes of the reciprocal AgBr-ACl systems at 0.5 mole fraction are found, within experimental error, to have a linear dependence on δ_{12}. The positive deviations from conformal solution theory which occur for the alkali halide mixtures have been interpreted in terms of non-Coulombic polarisation and van der Waals interactions.

Introduction

The integral molar excess functions of mixing G^E and S^E for the AgBr-ABr (A = Li, Na, K, Rb, Cs) systems have recently been shown[1] to be consistent with the Davis-Rice theory[2], which is an extension of the second order conformal solution theory[3] of Reiss, Katz, and Kleppa. Since V^E is related to G^E by $V^E = (\partial G^E/\partial P)_T$, it may be possible to apply conformal solution theory to the excess volumes of binary molten salt systems. This paper reports the excess volumes of the binary AgBr-ABr and the reciprocal AgBr-ACl (A = Li, Na, K, Rb, Cs) systems in order to investigate the possible functional dependence of V^E on the diameter difference parameter, δ_{12}, arising from the Reiss, Katz, Kleppa theory. Four alkali halide mixtures have also been investigated in order to determine the effect on V^E of exchanging bromide for chloride ions, or small cations for larger cations, and to aid comparison with published data.

Excess volumes of mixing are usually obtained from the densities of the mixture and pure components. While the direct method of Cleaver and Neil[4] provides the greatest accuracy when dealing with low melting point components, it is not readily adaptable to temperatures above 800 °K. Therefore in this investigation it was decided to use the Archimedean method for the density measurements since, provided corrections for air bouyancy and surface tension are applied, accuracies between 0.1 and 0.2% are attainable[5-7].

Experimental

Furnace. The 7 cm internal diameter core of the alumina tube furnace was wound with three sets of nichrome windings. The main windings, 26 ohms resistance, extended over the entire length of the core, with current being supplied from a Eurotherm 10 amp SCR proportionationg temperature controller. Two further windings, each of 50 ohms resistance, were situated at the top and bottom of the core to compensate for end losses. Two 2 amp variable A. C. transformers controlled the power to the latter two windings. This arrangement enabled a constant temperature zone of 0.1 °K over 10 cm at 1000 °K to be easily maintained. The furnace, being counterweighted, was designed to slide vertically over a length of 70 cm with negligible lateral movement. The position of the melt relative to the bob could be slowly and precisely adjusted by moving a lever clamped to the pulley supporting the counterweights.

Balance. A Mettler H14 balance was positioned on a vibration-free platform. The stirrup projecting through the floor of the balance was protected from draughts by a conical glass cover. A nichrome suspension wire inside a 3 cm diameter pyrex tube was used from the stirrup to the top of the furnace, and was connected to a 0.15 mm diameter platinum wire fastened to the bob. The latter, approximately 1 cm^3, consisted of a platinum cylinder sealed in a close fitting quartz envelope. The volume of the bob was accurately determined by measuring, on a semimicro balance, its weight loss when suspended in conductivity water at a known temperature. Corrections were applied for surface tension on the platinum suspension wire.

Sample Assembly. The melt was contained in a quartz tube resting on firebricks inside the tube furnace. Temperatures were measured with a Bureau

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of Standards calibrated chromel-alumel thermocouple inserted in a pocket on the side of the quartz sample holder. A unique feature of the assembly is a sliding 0-ring connector which fitted on top of the quartz tube. On moving the furnace, the connector enabled the pyrex tube enclosing the suspension wire to slide vertically inside the quartz tube, thereby altering the position of the melt relative to the bob, without moving the bob.

Salts. Great care was taken in purifying and handling the salts used, AgBr, LiBr, RbBr, CsBr (CERAC/PURE, 99.9%); NaBr and KBr (British Drug Houses Ltd., 99.9%) were further purified by heating under dynamic vacuum at 473 °K for 3 days, followed by treatment with a stream of freshly prepared dry hydrogen bromide for 2 hr while slowly raising the temperature to the melting point. Finally dry nitrogen was passed through the melt for 2 hr to remove all traces of the hydrogen bromide. AgCl, LiCl, NaCl, KCl (British Drug Houses Ltd., 99.8%); RbCl and CsCl (CERAC/PURE, 99.9%) were similarly treated, but with dry hydrogen chloride gas. The purified salts were stored in dark bottles in a dry box under an atmosphere of dry nitrogen, and all subsequent handling of the salts was performed in the dry box.

Procedure. Equimolar amounts of the components, sufficient to ensure a melt depth of 5 cm, were weighed directly into a quartz crucible. With the furnace at the bottom of its travel, the quartz tube containing the salts was fitted with the sliding connector and positioned in the furnace. A pyrex tube, 10 cm in length and 3 cm in diameter, closed at one end with two vacuum taps, was placed in the top of the connector so that the salts could be maintained under vacuum while the temperature was being raised to the melting points of the components. Dry nitrogen was admitted just below the melting point, so that melting took place under an inert atmosphere. After standing for 12 hr to allow for equilibration, the pyrex tube was quickly removed, and the bob and platinum suspension wire rapidly positioned. Finally the furnace was carefully raised until the bob entered the melt. Densities were measured on heating and cooling cycles, and in between temperature changes the furnace was lowered so that the bob was suspended in the nitrogen atmosphere 10 cm above the melt, in order to reduce chemical attack on the quartz envelope. The weight of the bob in the melt was also determined at different heights below the melt surface, to check for complete mixing of the components and/or temperature gradients. Corrections were applied for air bouyancy, surface tension, the thermal expansion of quartz (coefficient of cubical expansion 1.5×10^{-6} deg^{-1}), and for the immersion of the suspension wire if the length of wire in the melt differed from that during the volume calibration. If densities are measured at regularly increasing temperatures, then condensation of salt on the suspension wire cannot be detected, and this leads to low values for the densities. However, by measuring densities on successive stepwise heating and cooling cycles, deposition of salt on the wire could immediately be recognised by irreproducible results, and it was this factor that determined the temperature ranges listed in Table 1. The volume of the bob was redetermined at the completion of every system to check for chemical attack on the quartz. As soon as the volume of the bob had changed by 0.10 to 0.15% (usually after 4 systems) a new bob was made. Volume changes in the bob greater than 0.07% were never found to occur for any one particular system.

Table 1. Least squares fits for the densities fitted to Eq. (1) at 0.5 mole fraction.

System	a/gm cm^{-3}	$10^3\,b$/ gm cm^{-3} K^{-1}	Std. Dev.	Temp. Range, °K
AgBr-LiBr	4.743_9	0.892_8	0.0008	801 – 963
AgBr-NaBr	4.626_2	1.004_2	0.0009	922 – 1068
AgBr-KBr	4.345_2	1.028_0	0.0019	852 – 1087
AgBr-RbBr	4.727_5	1.156_6	0.0015	808 – 1052
AgBr-CsBr	4.993_8	1.272_3	0.0015	749 – 1077
AgBr-LiCl	4.343_1	0.859_2	0.0004	870 – 998
AgBr-NaCl	4.210_1	0.893_3	0.0006	974 – 1042
AgBr-KCl	3.966_3	0.931_7	0.0009	855 – 1074
AgBr-RbCl	4.434_5	1.104_6	0.0003	803 – 1075
AgBr-CsCl	4.705_6	1.180_9	0.0009	823 – 1091
AgBr-AgCl	5.973_8	1.009_7	0.0011	760 – 1037
KBr-NaBr	2.970_1	0.749_2	0.0009	1023 – 1114
KBr-CsBr	3.624_1	1.009_2	0.0002	980 – 1119
KCl-KBr	2.547_2	0.683_5	0.0004	1017 – 1125
KCl-CsBr	3.359_7	0.940_8	0.0009	933 – 1100

Results

The densities of pure AgBr were measured at 12 temperatures in the range 717 – 977 °K. The results agree with the values recommended by Janz[8] to within 0.05%. The results were fitted to the equation

$$\varrho = 6.321 - 1.050 \times 10^{-3}\,T$$

with a standard deviation of 0.0018. The measured densities of the mixtures were fitted to equations of the form

$$\varrho = a - b\,T \qquad (1)$$

where ϱ is in gm cm^{-3} and T in Kelvins. The coefficients a and b were calculated by the method of least squares, and are given in Table 1.

The excess volumes of mixing were calculated from the equation

$$V^{\mathrm{E}} = 1/\varrho \sum x_i M_i - \sum x_i M_i/\varrho_i$$

where ϱ is the density of the mixture, and ϱ_i, x_i, M_i are the density, mole fraction, and formula weight of the i th component respectively. Values of $V^{\mathrm{E}}_{0.5}$ at various temperatures for all the systems studied are given in Table 2. In calculating these values, the alkali halide densities used are those recommended by Janz[8]. The experimental precision of the results in Table 2 is estimated to be within ± 0.03 cm^3 mol^{-1}.

Table 2. Values of $V^{\mathrm{E}}_{0.5}$ at various temperatures for the halide melts.

System	$V^{\mathrm{E}}_{0.5}$, cm^3 mol^{-1}		
	923 °K	973 °K	1023 °K
AgBr-LiBr	−0.14	−0.15	−0.15
AgBr-NaBr	0.49	0.49	0.49
AgBr-KBr	0.53	0.53	0.53
AgBr-RbBr	0.63	0.63	0.63
AgBr-CsBr	0.74	0.77	0.80
AgBr-LiCl	0.60	0.61	0.62
AgBr-NaCl	0.98	0.99	1.00
AgBr-KCl	1.35	1.38	1.42
AgBr-RbCl	1.43	1.49	1.55
AgBr-CsCl	1.49	1.55	1.60
AgBr-AgCl	0.06	0.08	0.10
KBr-NaBr	0.35	0.28	0.21
KBr-CsBr	0.37	0.35	0.32
KCl-KBr	0.08	0.05	0.01
KCl-CsBr	0.19	0.18	0.17

Discussion

Comparison with previous data: Salstrom and Hildebrand[9–12] reported the following values of $V^{\mathrm{E}}_{0.5}$ (cm^3 mol^{-1}); AgBr-LiBr, −0.13 at 823 °K; AgBr-NaBr, 0.15 at 873 °K; AgBr-KBr, 0.28 at 873 °K; AgBr-RbBr, 0.42 at 873 °K, which are lower than the respective corresponding results of this study: −0.13; 0.49; 0.53; 0.63 cm^3 mol^{-1}. This is easily explained by the fact that the molar volumes of the alkali bromides used in their calculations of $V^{\mathrm{E}}_{0.5}$ were up to 0.23 cm^3 larger than the values recommended by Janz. Additional errors in their density measurements of the mixtures are attributed to their neglect of surface tension corrections. Boardman et al.[13] measured the densities of the AgBr-AgCl systems at various compositions using a dilatometer method, and found V^{E} to be zero at 873 °K within their limits of experimental accuracy, which agrees with the present result of $V^{\mathrm{E}}_{0.5} = 0.04$ at 873 °K.

Conformal solution theory: The second order conformal solution theory of Reiss, Katz, and Kleppa[3] gives the integral molar excess free energy of mixing as

$$G^{\mathrm{E}} = x_1 x_2 \theta(T,P)\,[(d_2 - d_1)/d_1 d_2]^2 = x_1 x_2 \theta(T,P)\,\delta_{12}{}^2$$

where x_i and d_i are the mole fraction and cation-anion separation of the i th component respectively, and $\theta(T,P)$ is a function of temperature and pressure only. Since V^{E} is related to G^{E} by $V^{\mathrm{E}} = (\partial G^{\mathrm{E}}/\partial P)_T$, then provided d_1 and d_2 are not pressure dependent,

$$V^{\mathrm{E}} = x_1 x_2 \Psi(T,P)\,\delta_{12}{}^2 \qquad (2)$$

where $\Psi(T,P)$ is again a function of temperature and pressure only. Cleaver and Neil measured V^{E} at 0.5 mole fraction for several binary alkali nitrate mixtures and found that the results could be fitted to the equation

$$V^{\mathrm{E}}_{0.5} = 22.5\,\delta_{12}{}^2 \qquad (3)$$

where $V^{\mathrm{E}}_{0.5}$ is in cm^3 mol^{-1} and δ_{12} in Å^{-1}. The nitrate systems containing $CsNO_3$ all exhibited positive deviations from Eq. (3), and it was suggested that this was due to van der Waals or polarisation interactions. Now since London – van der Waals forces between two cations are essentially proportional to $\gamma = |\alpha_1 \alpha_2 - \frac{1}{2}(\alpha_1{}^2 + \alpha_2{}^2)|$, where α_1 and α_2 are the polarisabilities of the two cations, then these interactions will rapidly increase in the order Cs-Rb < Cs-K < Cs-Na. This semi-quantitatively explains the $V^{\mathrm{E}}_{0.5}$ values of 0.02, 0.05, 0.17 cm^3 mol^{-1} for the $CsNO_3$-$RbNO_3$ ($\gamma = 0.41 \times 10^{-48}$ cm^6), $CsNO_3$-KNO_3 ($\gamma = 0.98 \times 10^{-48}$ cm^6), and $CsNO_3$-$NaNO_3$ ($\gamma = 2.33 \times 10^{-48}$ cm^6) systems respectively, measured by Cleaver and Neil. The value of γ for the KBr-NaBr system (0.29×10^{-48} cm^6) is considerably less than that of the KBr-CsBr system (0.98×10^{-48} cm^6), so that it would be expected that the KBr-CsBr system would have a larger V^{E} than the KBr-NaBr system, and this is confirmed by the data in Table 2.

The London – van der Waals interactions do not depend to any great extent on the anion (except for F^-, where the ionic radius is particularly small), but the polarisation interactions are strongly dependent on the nature of the anion. Lumsden[14] has shown that the polarisation forces are proportional to $\alpha(1/d_1^2 - 1/d_2^2)^2$, where α as the polarisability of the anion. Using anion polarisabilities of Tessman et al.[15] and the ionic radii of Goldschmidt[16], it is found that the polarisation interactions will increase in the order $NO_3^- < Cl^- \leqq Br^-$ for any pair of alkali cations. This may be illustrated, for example, with the KNO_3-$NaNO_3$ system[4] ($V^{E}_{0.5} = 0.01$ at 625 °K), the KCl-NaCl system[17] ($V^{E}_{0.5} = 0.23$ at 973 °K), and the KBr-NaBr system ($V^{E}_{0.5}0.28$ at 973 °K) in this study.

The two alkali halide reciprocal systems which were investigated show a similar trend, with the KCl-CsBr system having a larger positive V^E than the KCl-KBr system. The common cation – mixed anion systems which were investigated, AgBr-AgCl and KCl-KBr, both have excess volumes very close to zero. These small deviations from ideality were found to be characteristic of common cation – mixed anion mixtures by Melnichak and Kleppa[18] who found only small heats of mixing for the AX-AY (A = Li, Na, K, Rb, Cs; X, Y = Cl, Br, I) systems.

The $AgNO_3$-ANO_3 and $TlNO_3$-ANO_3 systems studied by Cleaver and Neil[4] deviated from Eq. (3) to the extent that the systems showed large positive values of V^E even when δ_{12} was close to zero. Attempts to explain this using the Davis-Rice theory[2] together with van der Waals forces and polarisation interactions were unsuccessful, so that Cleaver and Neil were forced to conclude that there must be further factors involved which are not taken into account by the Davis-Rice theory. It was suggested that there might be a degree of covalent character in the bonding between Ag^+ or Tl^+ and NO_3^-. Addition of $LiNO_3$ to $AgNO_3$ or $TlNO_3$ would probably reduce the amount of covalent character, while the addition of Na, K, Rb, Cs nitrate should enhance the covalent character. This concept was used by Thurmond[19] to interpret the thermodynamic behaviour of the AgBr-ABr systems, and later by Kleppa et al.[20–22] who showed that the degree of covalent character would increase in the order

$$TlNO_3\text{-}ANO_3 < AgNO_3 - ANO_3 < TlCl\text{-}ACl < AgCl\text{-}ACl < AgBr\text{-}ABr$$

Values of $V^{E}_{0.5}$ in Table 2 show that large positive deviations exist for the AgBr-ABr systems, and that they increase in the order Na, K, Rb, Cs. In the AgBr-LiBr system the AgBr covalent character appears to be reduced to the extent that $V^{E}_{0.5}$ is negative.

This concept of covalent bonding increasing with the size of the alkali cation has been strongly supported by the NMR chemical-shift data on molten thallium halide – alkali halide systems reported by Hafner and Nachtrieb[23]. It was found that the downward chemical shift of the Tl^{205} nucleus in thallium halide – alkali halide mixtures increases in the order Li < Na < K < Rb < Cs, and this was attributed to increases in the covalent character of the thallium – halide bond. However, recent excess volume data for the TlBr-ABr (A = Na, K, Rb) systems[24, 25] and the TlCl-KCl and TlCl-RbCl systems[26] has indicated that V^E increases positively in the order Rb < Na < K for the TlBr-ABr mixtures, and in the order Rb < K for the TlCl-ACl mixtures. Buckle and Tsaoussoglou[25], in the order to account for this anomalous behaviour, concluded that there must be some structural effects not detected by NMR that influence the molar volumes of the thallium mixtures. No such structural effects are indicated for the AgBr-ABr systems in this study, or for the $TlNO_3$-ANO_3, $AgNO_3$-ANO_3 systems[4] studied by Cleaver and Neil.

The Reiss, Katz, Kleppa theory[3] strictly applies to solutions having a common cation or common anion. However, we find that the V^E data in Table 2 for all five reciprocal AgBr-ACl systems can be fitted, within experimental error, to a linear function in δ_{12}, yielding

$$V^{E}_{0.5} = 1.06 - 8.4\,\delta_{12} \qquad (4)$$

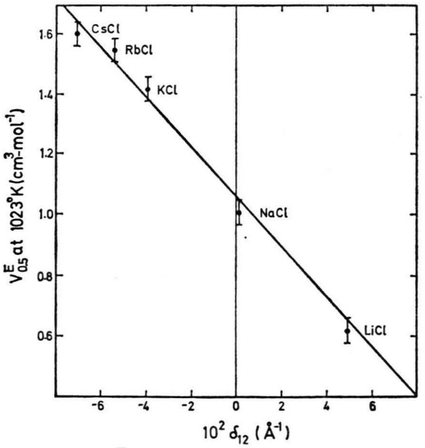

Fig. 1. Values of $V^{E}_{0.5}$ at 1023 °K for the reciprocal AgBr-ACl (A = Li, Na, K, Rb, Cs) systems plotted against δ_{12}.

where δ_{12} is in Å^{-1}, as shown in Figure 1. The interionic distances in the melts estimated by Melnichak and Kleppa[22] for the alkali chlorides, and the recently suggested[27] value of $d_{\text{AgBr (liquid)}} =$ 2.80 Å, have been used in the calculation of δ_{12}.

Equation (4) represents an empirical relationship for which no explanation in structural terms is apparent.

The excess volumes of the AgBr-ABr systems in Table 2 are found to be independent of temperature within experimental error, while the excess volumes of the AgBr-ACl systems in Table 2 show a slight increase with increasing temperature, and this effect becomes greater as the size of the alkali cation increases. This is in contrast with the four alkali halide systems in Table 2 where $V^{\text{E}}_{0.5}$ decreases significantly with increasing temperature. With the limited data available, it is not possible to account for the manner in which the excess volumes of the various systems vary with temperature.

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