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IN CALCIUM-ALKALI BROMIDE SOLUTIONS

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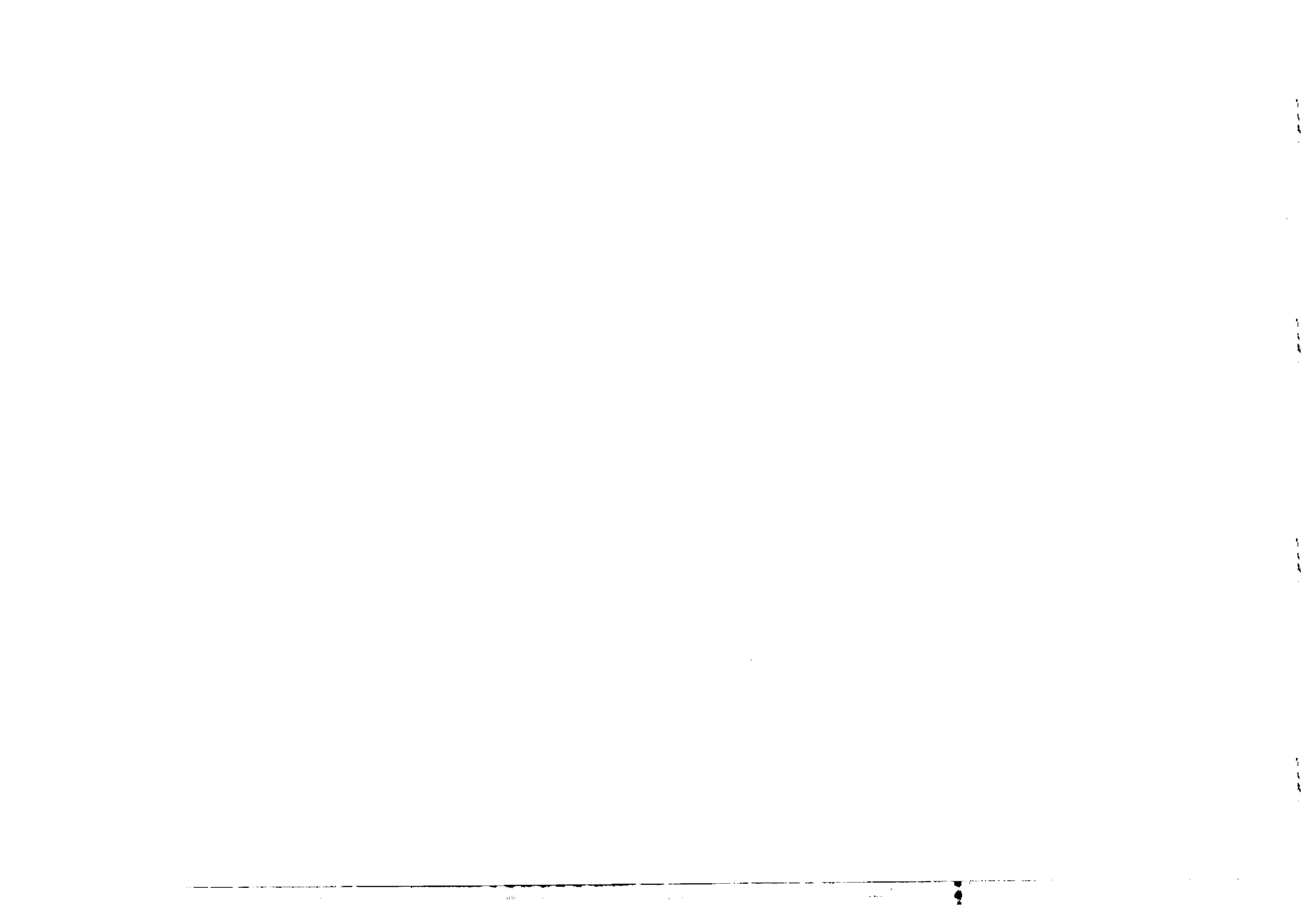and

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ABSTRACT

We discuss the dependence of the stability of tetrahedral complexes in molten halide mixtures on the halogen species. This is done by calculating the equilibrium concentration of $(CaBr_4)^{2-}$ complexes in calcium-alkali bromide solutions as a function of composition, in comparison with earlier calculations on the calcium-alkali chloride systems. The comparison supports a possible trend of increasing stability from chlorides to bromides, provided that halogen polarizability or chemical bonding contribute appreciably to the binding of a complex. Supporting evidence is noted and further experiments are suggested.

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1. Introduction

There is ample experimental evidence for a definite trend in the stability of tetrahedral halocomplexes in dependence on the alkali counterion species in liquid mixtures of polyvalent metal halides and alkali halides. In particular, greater stability in the presence of the heavier alkalis is most clearly revealed by the Raman scattering experiments of Sakai et al[1] and the thermochemical measurements of Østvold[2] on calcium - alkali chloride solutions. These experiments show stable $(CaCl_4)^{2-}$ complexes when the alkali counterion is Rb or Cs, no evidence of complexes with Li or Na, and coexistence of tetrahedral-type and octahedral-type configurations for Ca in partnership with K in molten $CaCl_2.2KCl$. The observed trend has been accounted for by calculations based on a simple ionic model[3]. The physical argument drawn from the theory is that, in a Mott viewpoint for the complex as a bound state in a conductor, its stability increases with the ratio $1/r_{CaCl}$ between the screening length 1 of the solution and the bond length r_{CaCl} of the complex. In going from the LiCl to the CsCl solvent, 1 increases while r_{CaCl} remains essentially constant.

The dependence of complex stability on the halogen species is evidently a more subtle question, since both the screening length and the bond length increase with increasing halogen ion size. Comparison of the two lengths for alkaline earth halides in all alkali halide solvents nevertheless suggests some increase of complex stability through the series from the fluoride to the iodide[4]. This appears to be consistent with the available evidence, although the problem has not as yet been studied experimentally in a fully systematic way. There is very extensive evidence on chlorides, some evidence on fluorides and bromides, and very little evidence on iodides.

The systems of foremost interest should again be the Mg, Ca and Sr halide solutions, which may show a transition between different preferred types of coordination for the polyvalent metal ion as the halogen species is changed at

constant alkali counterion. A preliminary comparison between various data on fluorides, chlorides and iodides can already be made. Specifically, the relevant observations are (i) an increase in the concentration dependence of the so-called interaction parameter extracted from data on the enthalpy of mixing[2,5,6] and (ii) the presence of a shoulder in the Raman scattering spectrum of a Ca - Li bromide mixture[7] suggesting that some of the Ca ions may be present in fourfold coordination by bromines.

The above considerations have motivated us to examine in greater theoretical detail the stability of tetrahedral complexes in calcium - alkali bromide mixtures within the same ionic model that has been previously used[3] for the chloride mixtures. In spite of the crudeness of the model, a physically meaningful comparison between the two series of systems is set up with the help of recent and more refined calculations on complexes in vacuo[8]. The results emphasize the role that experimental studies of the Ca - Li and Ca - Na bromide systems may have in relation to the question at hand and allow indirect conclusions on the nature of bonding in complexes in molten mixtures.

2. Description of the model and numerical results

As in the earlier work by two of us[3], the $(CaBr_2)_c$ - $(ABr)_{1-c}$ mixture (with A = any alkali) is treated as a four-component fluid consisting of tetrahedral $(CaBr_4)^{2-}$ complexes in molar fraction xc, free Ca^{2+} and Br^- ions in molar fractions $(1-x)c$ and $1 + (1 - 4x)c$, and A^+ alkali counterions. The equilibrium value of x follows from minimization of the Helmholtz free energy as the solution of the law - of - mass - action equation

$$\frac{x}{(1-x)(1+c-4xc)^4} = \left[\frac{M_{Ca}+4M_{Br}}{M_{Ca}M_{Br}^4}\right]^{3/2}\left[\frac{h^2}{2\pi k_B T v^{2/3}}\right]^6 \exp\left[-\frac{f(x)}{k_B T}\right] \quad (1)$$

where the M's are the ionic masses, v is the molar volume and

$$f(x) = f_c + \frac{1}{c}\left[\frac{\partial F_{ex}(x)}{\partial x}\right]_{T,v} \quad (2)$$

Here, f_c is the internal free energy of a complex relative to isolated ions and F_{ex} is the excess free energy of the liquid mixture arising from the interactions between its components. These free energies are evaluated by means of a charged-hard-spheres model, the mean spherical approximation (MSA) being adopted for the fluid. Use is made of recent estimates of vibrational mode frequencies for isolated complexes[8] in estimating the vibrational contribution to f_c, with only minor numerical changes relative to its earlier estimate in ref. 3.

Equations (1) and (2) are correct on the assumption that complexes are long - lived entities. However, the estimate of $f(x)$ is quite crude and requires a careful choice of the model parameters, especially for the purpose of comparing different halide systems. Considering the bromide systems at the same temperature T = 943 K as the chloride systems, we find that the MSA equation of state of the pure molten salt components is satisfied with the same values for the hard sphere diameters σ_A of alkali ions and σ_{Ca} of the Ca ion as reported in ref. 3, when the choice $\sigma_{Br} = 3.29$ Å is made for the diameter of Br$^-$ against the value $\sigma_{Cl} = 3.02$ Å for Cl$^-$. Such a difference between the two halogen ion sizes is consistent with all tables of ionic radii in the literature, including that given for molten alkali halides by Senatore et al[9], and immediately yields through the MSA equations that the screening length increases by about 6% in going from each alkali chloride to the corresponding bromide.

The other important length in the problem is the bond length r_{CaBr} in the complex, which determines the dominant contribution to f_c from Coulomb energy binding. By scaling the value adopted in ref. 3 for f_c in the chlorides with the help of binding energy calculations[8] for isolated $(CaCl_4)^{2-}$ and $(CaBr_4)^{2-}$ complexes, we

find that f_c should decrease in absolute magnitude by no more than 4% in going from the chloride to the bromide. In terms of effective bond lengths in the model, this implies that r_{CaBr} should be larger than r_{CaCl} by at most 0.1 Å. We stress that the difference between the two effective bond lengths is smaller than the difference in geometrical sizes of bromine and chlorine ions, which is $(\sigma_{Br} - \sigma_{Cl})/2$. The reason is that binding of complexes in the isolated state includes a sizable contribution from halogen polarization[8], which is appreciably larger in $(CaBr_4)^{2-}$ than in $(CaCl_4)^{2-}$. On the other hand, such polarizability contributions are known[10] to be very minor in the excess free energy of molten salts.

On the basis of the foregoing assessment of model parameters and starting from the value $r_{CaCl} = 2.36$ Å adopted in ref. 3 for the effective bond length in $(CaCl_4)^{2-}$, we have carried out calculations for the bromide systems with two alternative choices for the effective Ca - Br bond length, which are $r_{CaBr} = 2.46$ Å and $r_{CaBr} = 2.40$ Å. The results for the equilibrium fraction of complexes as a function of concentration are shown in Figures 1 and 2, respectively. Of course, the trend of increased complex stability with heavier alkali partners is fully confirmed. Figure 1 shows that the choice $r_{CaBr} = 2.46$ Å yields for the bromides a situation which is entirely similar to that of the chlorides. In particular at $c = 1/3$ an intermediate state of partial fourfold coordination is found for the Ca ion in partnership with K, separating full stability of complexes with Rb or Cs counterions at this composition from instability of complexes with Na or Li counterions. On the other hand, some further enhancement of $(CaBr_4)^{2-}$ binding, as seen in Figure 2 for $r_{CaBr} = 2.40$ Å, would drive the system to a mixed coordination state for Ca in $CaBr_2.2NaBr$ and would preserve a fraction of fourfold coordinated Ca ions in partnership with Li over a range of mixture composition.

3. Concluding remarks

We have seen that, provided that halogen polarizability or chemical bonding contribute to the binding of calcium halide complexes in liquid mixtures to the extent which is suggested by calculations on complexes in the isolated state, their stability in bromide mixtures is at least as strong as in chloride mixtures and possibly somewhat stronger. In particular, the replacement of chlorine with bromine could counterbalance the loss of stability which is met in the chloride mixtures upon replacing potassium with sodium or lithium.

It would clearly be useful to have detailed experimental studies and data analyses for the systems that we have evaluated, in addition to the available thermochemical data. More generally, systematic experimental investigations of complex stability with varying halogen species would be of great interest.

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Figure captions

Figure 1. Equilibrium value of complex fraction versus solute concentration for $CaBr_2$ in alkali bromide solvents, for $r_{CaBr} = 2.46$ Å. The broken line shows the highest allowed value of x_{eq} for $c > 1/3$.
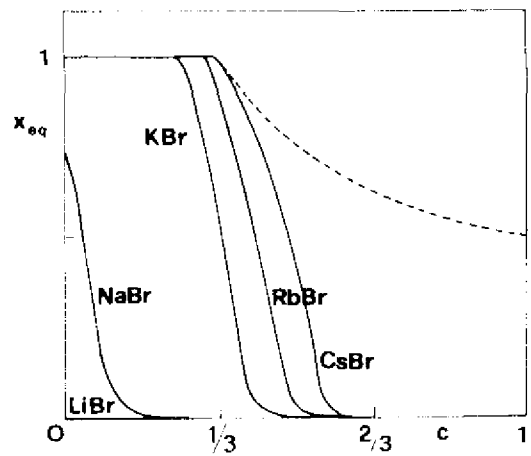
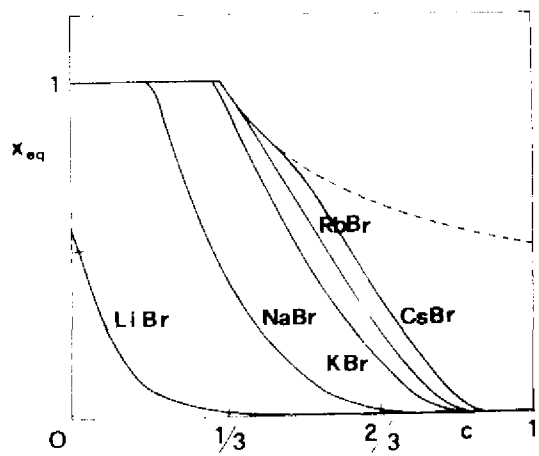**Figure 2.** Same as in Figure 1, for $r_{CaBr} = 2.40$ Å.

Fig.1

Fig.2