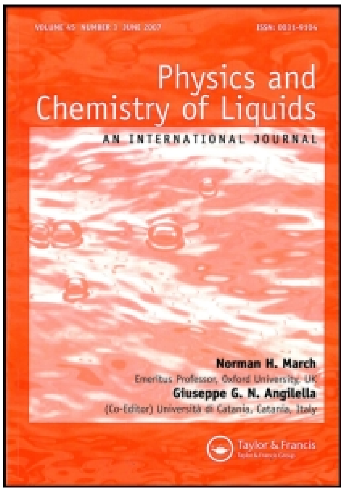

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Stability of Chlorocomplexes in Molten Salt Mixtures as a Screening-controlled Chemical Equilibrium

Z. Akdeniz[a]; M. P. Tosi[b]
[a] Faculty of Science and Letters, Istanbul Technical University, Maslak, Istanbul, Turkey [b] Dipartimento di Fisica Teorica del/'Università and International Centre for Theoretical Physics, Trieste, Italy

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Stability of Chlorocomplexes in Molten Salt Mixtures as a Screening-controlled Chemical Equilibrium

Z. AKDENIZ

Faculty of Science and Letters, Istanbul Technical University, Maslak, Istanbul, Turkey.

and

M. P. TOSI

Dipartimento di Fisica Teorica dell'Università and International Centre for Theoretical Physics, Trieste, Italy.

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We develop a simple ionic model for solutions of polyvalent cation chlorides in molten alkali chlorides, which allows for the possible formation of long-lived tetrahedral chlorocomplexes in chemical equilibrium with free species. Complex stability is evaluated as a function of the alkali chloride solvent and of solute concentration c, the relevant free energies being determined from charged hard sphere interactions with parameters adapted to simulate a calcium chloride solute. For a given binding free energy of complexes, their stability is controlled by the ionic screening length of the solution. In particular, we find (i) instability of calcium chlorocomplexes in lithium chloride solvent, marginal stability at low c in sodium chloride solvent and increasing stability through the series of solvents from potassium to cesium chloride; and (ii) rapid dissociation of complexes in each of these latter solvents with increasing solute concentration as c goes through or exceeds the "stoichiometric" composition $c = \frac{1}{3}$. The dissociation process is driven by a positive-feedback screening mechanism, the decrease of the screening length with increasing c being primarily determined by free calcium ions. Dissociation of complexes may therefore be viewed as a classical insulator-to-conductor transition, which occurs in a narrow range of composition in correspondence to a "critical value" of the screening length. A stability criterion for complexes is derived and contact is made with the available evidence from thermodynamic and Raman spectroscopy data.

Key Words: Stable chlorocomplexes, screening-controlled chemical equilibrium.

1 INTRODUCTION

A broad variety of measurements on molten mixtures of polyvalent cation halides and alkali halides indicate that a polyvalent cation may locally coordinate halogen ions into a fourfold configuration, such a unit being often viewed as a "complex" surrounded by alkali "counterions". The best known example is probably that of mixtures of $AlCl_3$ and alkali chlorides. The existence of well defined $(AlCl_4)^-$ tetrahedral configurations in these systems, which has been known for a long time from thermodynamic and Raman spectroscopy data, has been directly revealed recently in the $LiCl$–$AlCl_3$ system at equimolar composition by neutron scattering experiments carried out by Biggin *et al.*[1] Such tetrahedral configurations have also been widely proposed in the literature for solutions of other trivalent or divalent cation chlorides, such as YCl_3 or $BeCl_2$ and $MgCl_2$, in molten alkali chlorides.

A number of counterexamples, however, are also known. We refer for instance to the recent Raman spectroscopy work of Sakai *et al.*[2] which failed to reveal complexes in the systems $CaCl_2$–$2LiCl$, $CaCl_2$–$2NaCl$, $SrCl_2$–$2KCl$ and $SrCl_2$–$2RbCl$. The $CaCl_2$–$2KCl$ system appears from this work to be of very special interest, insofar as the data analysis given by Sakai *et al.* indicates coexistence of sixfold-coordinated and fourfold-coordinated configurations for the calcium ions. This observation suggests coexistence of "free" and "complexing" Ca^{2+} ions, at a composition where the number of chlorine ions in the mixture is just such that complete coordination of all calcium and chlorine ions into $(CaCl_4)^{2-}$ complexes would be allowed.

On the theoretical side, little is known about the stability of tetrahedral configurations as a function of the "solute" (the polyvalent cation halide), the "solvent" (the alkali halide) and the composition of the mixture. Quantum chemistry methods have been usefully applied[3] to $(AlCl_4)^-$ and $(Al_2Cl_7)^-$ species, both in the free state and in the presence of a few model external charges, for evaluations of structure and vibrational frequencies. However, a combination of these methods with a statistical mechanical account of many-body effects in the liquid solution has not yet been attempted. Definite encouragement towards developing a statistical mechanical theory of complexing liquid mixtures has come from recent work of Saboungi *et al.*[4] These authors have simulated an $AlCl_3$–$NaCl$ mixture at a few compositions by molecular dynamics methods and shown that a simple ionic model of the melt can reproduce structural features of a complexing liquid that are usually assigned to covalency. Their results considerably strengthen earlier theoretical suggestions[5] regarding the origin of local coordinations for transition metal ions at high dilution in molten alkali halides. It can also be inferred, from the existence of empirical correlations between thermodynamic data and simple parameters describing the various ionic interactions in such liquid mixtures[6], that the above conclusion ought to have fairly general qualitative validity.

We examine in this paper a statistical mechanical model of divalent cation-alkali chloride mixtures at varying concentration c of the divalent chloride solute. The model is assuredly crude but nevertheless significant. It rests on the following assumptions:

(i) a fraction x of the divalent cations at each composition c can form tetrahedral complexes if this lowers the free energy relative to that of a liquid containing only free ionic species, and in this case the complexes are an equilibrium species with a lifetime which is long compared with typical times for diffusion and rotation;

(ii) all interactions are described by representing the ions as charged hard spheres, both within each complex and as components of the mixture;

(iii) the free energy of the mixture, which is to be minimized as a function of x for each composition c, is evaluated in the mean spherical approximation (MSA) of Waisman and Lebowitz[7,8]. The model neglects changes in the internal structure of complexes with composition of the solution, which are expected to be small[3], and the possible formation of larger bound complexes.

With regard to points (ii) and (iii) above, we should remark here that we have adjusted the model for calculational purposes to calcium-alkali chloride mixtures by reference to properties of the pure components and also to the aforementioned observation of Sakai *et al.*[2] on the $CaCl_2$-$2KCl$ system. The latter allows us a rough assessment of the binding free energy of a $(CaCl_4)^{2-}$ complex and of its size, with results which, as we shall see, are grossly consistent with an ionic description of the complex within an ionic liquid matrix. With regard to point (i), on the other hand, we note that one may expect an active dynamics of complex formation and dissociation when the equilibrium value of x is appreciably different from zero or unity. This feature appears in our calculations through the flatness of the free energy as a function of x around its minimum, in a range of composition where we find that complexes are rapidly becoming unstable.

The main qualitative value of the model is to demonstrate a precise correlation between the complexing behaviour and the ionic screening length of the liquid, for a given binding free energy of a complex. A "critical value" of the screening length, as appropriately defined in the MSA for a liquid of charged hard spheres, appears to be involved. Let us anticipate here our results for the two extreme cases of $CaCl_2$ in LiCl and in CsCl. The ionic screening length in pure LiCl is sufficiently short that complexes are unstable even in the limit of vanishing concentration of divalent cations, whereas in CsCl all divalent cations are present in complexes up to $c = \frac{1}{3}$. At higher concentrations, however, the highest allowed value of x is $(1 + c)/4c$: some of the calcium ions are necessarily free and induce a progressive shortening of the screening length and hence a progressive decrease of the stability of complexes. In the event, dissociation of all complexes takes place over a narrow range of composition. All the results of our calculations on complex stability can be summarized into a simple stability criterion, stating that the ratio between the length over which a complex is screened by the ionic liquid and the divalent cation-chlorine distance within the complex must be larger than about 1.6 for complexes to be stable up to $c \approx \frac{1}{3}$. There is an obvious parallelism between this view of complex dissociation and a classical insulator-to-conductor transition, such as the superionic transition in crystalline $SrCl_2$ and other fluorite-type materials.

The outline of the paper is briefly as follows. In Section 2, with the supplement of an Appendix, we give the essential equations of the theory and describe our assessment of the relevant parameters of the model. The main numerical results on complex stability are reported in Section 3, leading to the formulation of a stability criterion for complexes and a comparison with the Raman spectroscopy evidence on alkaline earth-alkali chlorides. Finally, section 4 discusses comparisons with thermodynamic data on the heat of solution, as well as the usefulness of excess volume and heat capacity measurements in relation to the process of complex dissociation with increasing concentration.

2 DESCRIPTION OF THE MODEL

We consider the liquid mixture $(MX_2)_c$-$(AX)_{1-c}$, where M denotes a divalent cation, A an alkali ion and X a halogen ion, at a molar volume v which is fixed by linear interpolation between the molar volumes of the pure components as reported by Janz[9]. The system is regarded as a four-component fluid consisting of $(MX_4)^{2-}$ complexes (molar fraction $= xc$), M^{2+} ions (molar fraction $= c - xc$), X^- ions (molar fraction $= 1 + c - 4xc$) and A^+ ions (molar fraction $= 1 - c$).

The Helmholtz free energy F, aside from an irrelevant additive constant, can be written as

$$F = xcf_c - TS_m(x) + F_t(x) + F_{ex}(x) \tag{2.1}$$

where f_c is the binding free energy of the complex relative to free ions in vacuo, $S_m(x)$ is the ideal entropy of mixing, $F_t(x)$ is the free energy associated with translational motions of all the components of the fluid and $F_{ex}(x)$ is the excess free energy arising from interactions between the components. From the expression

$$\begin{aligned} S_m(x) = &-k_B\{xc\ln(xc) + (1-c)\ln(1-c) \\ &+ (1+c-4xc)\ln(1+c-4xc) \\ &+ (c-xc)\ln(c-xc) - (2+c-4xc)\} \end{aligned} \tag{2.2}$$

we find upon minimization of F with respect to x that the equilibrium value of x is determined by the equation

$$\frac{x}{(1-x)(1+c-4xc)^4} = A\exp[-f(x)/k_BT] \tag{2.3}$$

where

$$f(x) = f_c + (\partial F_{ex}(x)/\partial x)_{T,v}/c \tag{2.4}$$

and

$$\begin{aligned} A &= \exp[-(\partial F_t(x)/\partial x)_{T,v}/ck_BT] \\ &= (M_C/M_M M_X^4)^{3/2}(h^2/2\pi k_BT)^6 v^{-4} \end{aligned} \tag{2.5}$$

the M's being the masses of the components (with C = complex). Clearly, Eq. (2.3) has the form of the law of mass action for the reaction

$$(MX_4)^{2-} \leftrightarrow M^{2+} + 4X^- \tag{2.6}$$

taking place in a condensed medium, which influences the reaction through the excess free energy contribution to the "activation free energy" $f(x)$. Of course, the role played by the alkali ion species is also contained in this contribution.

We adopt now a charged-hard-sphere description of the interactions in order to evaluate the free energies f_c and F_{ex}. We can then write the former as

$$f_c = V_c + f_{rot} + f_{vib} \tag{2.7}$$

where the internal Coulombic energy V_C is given for a tetrahedral structure of the complex by

$$V_c = [-8 + 6(\tfrac{3}{8})^{1/2}]e^2/r_{MX} \tag{2.8}$$

r_{MX} being the M–X distance within the complex. The rotational contribution f_{rot} is easily expressed through r_{MX} for a free rotator, while the vibrational contribution f_{vib} is determined by the nine vibrational frequencies of the complex. For an initial order-of-magnitude estimate, that we shall try to refine later, we estimate $r_{\mathrm{CaCl}} \approx 2.3$Å from the measured Zn–Cl distance in tetrahedrally coordinated molten $ZnCl_2$⁽¹⁰⁾ and assume nine vibrational modes at the measured Raman frequency $\nu = 224\,\mathrm{cm}^{-1}$ for the $(CaCl_4)^{2-}$ complex in the $CaCl_2$–2KCl system⁽²⁾. This yields $f_c \approx -670$ kcal/mole at $T = 943$ K, this magnitude being dominated by the Coulombic term. It is clear that there must be massive cancellations arising from the excess free energy of the mixture.

The excess free energy is evaluated for charged-hard-sphere interactions as the sum of a hard-core contribution and a Coulombic contribution,

$$F_{\mathrm{ex}}(x) = F_{\mathrm{hs}}(x) + F_C(x) \tag{2.9}$$

the detailed MSA expressions for these quantities being reported in the Appendix. These expressions involve four parameters, which are the hard-sphere diameters σ_M, σ_A, σ_X and σ_C for the four components of the liquid. The important point that we wish to stress here is that the MSA introduces in a natural way an ionic screening length for the dense ionic fluid, which determines both the excess Coulombic energy and the effective length of the dipole layer which is created in the screening of an external charge by the model ionic conductor[11,12]. The inverse of this screening length, for the case when the external charge is distributed on a planar wall, is commonly denoted in the MSA as 2γ (see Appendix). The effective length over which a complex is screened by the surrounding ionic liquid is of more direct interest for our purposes, and this screening length can be calculated as

$$l = (1 + \gamma\sigma_c)/2\gamma \tag{2.10}$$

The ratio l/r_{MX} suggests itself as a simple and physically significant parameter for measuring the balance between the binding of the complex and the Coulombic energy of the liquid.

Table 1 collects the values that we have adopted for the parameters of the model in our calculations on the calcium-alkali chloride systems at $T = 943\,K$[13]. The diameters σ_{Cl}, σ_A and σ_{Ca} were fixed by the requirement that the pressure-volume product for the pure components, as determined in the MSA, should be essentially negligible compared with k_BT. For the alkali and chlorine ions these values are mostly quite close to those determined by Senatore *et al*[14] by fitting the measured compressibility of molten alkali halides with the same MSA expression for the excess free energy. The precise value of the effective diameter σ_C of the complex is not crucial in our calculations, and we have related it to the Ca-Cl distance within the complex by the relation

$$\sigma_C = (\tfrac{8}{3})^{1/2} r_{MX} + \sigma_X \tag{2.11}$$

which is somewhat less than appropriate for a freely rotating tetrahedron. Finally, for an assessment of f_c and r_{CaCl} we have required that the results of the theory should be consistent with the observations of Sakai *et al*[2] yielding comparable numbers of sixfold and fourfold-coordinated calcium ions (i.e. $x \approx 0.5$ at equilibrium) in calcium-potassium chloride at $c = \frac{1}{3}$ and $T = 943$ K. This yields $f_c = -653.5$ kcal/mole at this temperature and, on reversing the argument that led to our earlier estimate of f_c, we find $r_{CaCl} = 2.36$ Å. As a gauge of the absolute reliability of this latter value, we may quote again the measured value of r_{ZnCl} in tetrahedrally coordinated molten zinc chloride ($r_{ZnCl} =$ 2.29Å[10]) and also the measured value of the Ca-Cl distance in the $CaCl_2$ molecule ($r_{CaCl} = 2.51$ Å[15]). In spite of this latitude we have some confidence that, having treated on the same footing the binding of the tetrahedral configuration and the interactions in the liquid mixture, internal consistency has been achieved to a useful extent in the choice of the model parameters.

3 NUMERICAL RESULTS ON STABILITY OF COMPLEXES

Figure 1 reports our results for the equilibrium value of the fraction x of complexes and for the corresponding value of the inverse screening length 2γ of the solution as functions of composition in the five alkali chloride solvents. The following features are immediately evident.

(i) In the limit of infinite dilution ($c \to 0$) we find that complexes are unstable in LiCl, partially stable in NaCl and fully stable in KCl, RbCl and CsCl. Their stability correlates with the magnitude of $(2\gamma)^{-1}$ for the pure molten alkali chloride. The latter is determined primarily by the size of the alkali ion.

(ii) While complexes in NaCl become rapidly unstable with increasing solute concentration, they remain fully stable in KCl, RbCl and CsCl over a finite range of composition. The screening length increases steadily over this composition range as Cl^- ions are increasingly taken out of the solution and bound by Ca^{2+} ions.

(iii) The concentration at which partial complex stability sets in correlates again with the magnitude of $(2\gamma)^{-1}$ in the pure solvent. The transition from $x = 1$ to $x = 0$ is fast and is accompanied by a rapid

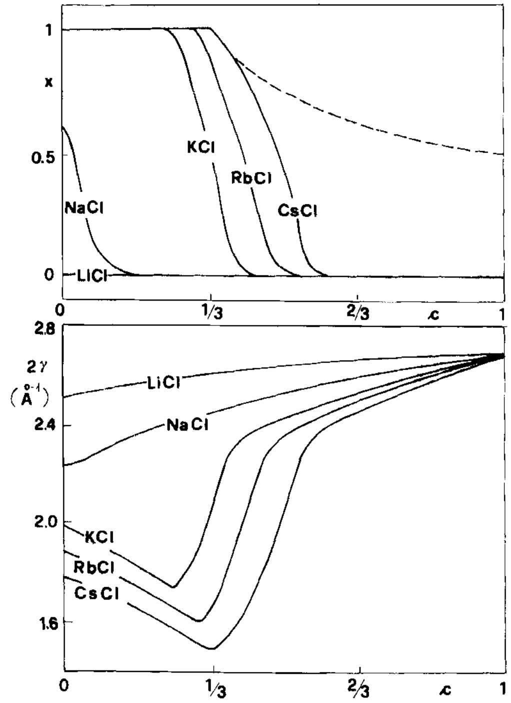

Figure 1 Equilibrium value of complex fraction x (top) and inverse screening length 2γ (bottom) versus solute concentration c for $CaCl_2$ in alkali chloride solvents. The broken line shows the highest allowed value of x, given by $(1 + c)/4c$ for $c \geq \frac{1}{3}$.

decrease of the screening length of the solution. In the CsCl solvent, in particular, the screening length starts decreasing at $c = \frac{1}{3}$ but the equilibrium value of x follows for a while the maximum allowed value above $c = \frac{1}{3}$ ($x = (1 + c)/4c$, shown by the broken line) before rapid dissolution sets in.

Figure 2 shows for the $CaCl_2$-KCl system that the sharpness of the transition is determined primarily by the contribution of free calcium ions to the screening length of the solution. We have here arbitrarily diminished the value of σ_{Ca} from 2.55 Å to 2.24 Å and adjusted the value of f_c so as to preserve the location of the transition at $c \approx \frac{1}{3}$. The role of free calcium ions in determining the screening length of the solution is increased and the transition from the bound to the dissolved state is correspondingly much sharper (although it is still continuous). Conversely, one might expect a smoother transition in the presence of covalency.

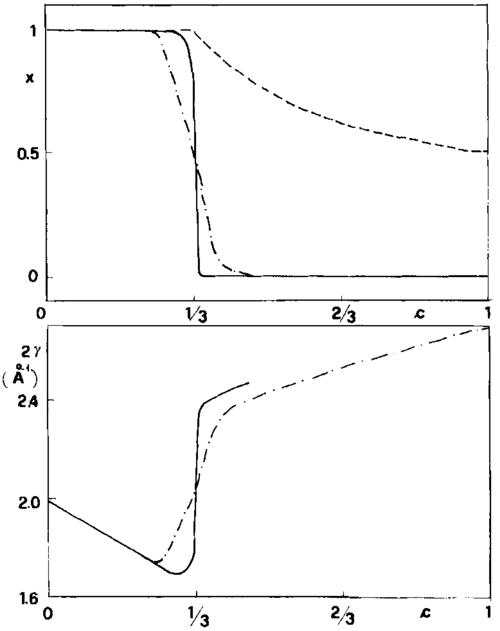

Figure 2 Same as Figure 1 for $CaCl_2$ in KCl, before (dash-dotted line) and after (full line) changing σ_{Ca} and f_c as described in the text.

The above correlations between the complexing behaviour of the solution and its inverse screening length immediately suggest that the stability of complexes is governed by a "critical value" of the screening length, which can be estimated from the results shown in Figure 1 for a given value of the binding free energy f_c. We estimate $\gamma_{crit} \approx 1.1$ Å^{-1} from both the behaviour of the different solvents at vanishing solute concentration and the behaviour of the dissociation process in KCl, RbCl and CsCl. A more general criterion for the stability of complexes can be obtained from the ratio of the screening length l, defined in Eq. (2.10), to the M-X distance within the complex. The former quantity accounts for the finite size of the complex in its screening by the solution and the latter, as we have seen in Section 2, is a gross measure of f_c in an ionic model. Table 2 shows the values of the ratio l/r_{MX} for all the alkaline earth-alkali chloride systems. We have here made use of Eqs (2.10) and (2.11), taking r_{MX} equal to the measured M-X distance in MX_2 molecules[15], γ from the MSA theory of the pure solvent at 943 K and σ_{Cl} from Table 1. Our results for the calcium-alkali chloride systems suggest

$$(l/r_{MX})_{crit} \approx 1.6 \qquad (3.1)$$

Table 1 Parameters of the model for calcium-alkali chloride solutions at $T = 943\,K$.

σ_{Cl} (Å)	σ_{Li} (Å)	σ_{Na} (Å)	σ_{K} (Å)	σ_{Rb} (Å)	σ_{Cs} (Å)	σ_{Ca} (Å)	σ_{C} (Å)	f_C (kcal/mole)
3.02	1.84	2.22	2.66	2.87	3.11	2.55	6.88	−653.5

Table 2 Values of the ratio l/r_{MX} for alkaline earth-alkali chlorides and predicted separation into complex-forming (above line) and non-forming (below line) systems.

	Li	Na	K	Rb	Cs
Be	1.93	1.96	1.99	2.01	2.03
Mg	1.69	1.71	1.74	1.75	1.77
Ca	1.58	1.60	1.62	1.63	1.64
Sr	1.53	1.55	1.57	1.58	1.60
Ba	1.49	1.51	1.53	1.54	1.55

as the critical ratio above which complexes are stable over a range of solute concentration extending up to $c \approx \frac{1}{3}$. As shown by the full and broken lines drawn inside Table 2, this criterion predicts stability of complexes for $BeCl_2$ and $MgCl_2$ in all the alkali chloride solvents and for $CaCl_2$ in KCl, RbCl and CsCl solvents, and marginal stability in the systems $CaCl_2$–NaCl and $SrCl_2$–CsCl. The above prediction is in nice agreement with the body of Raman spectroscopy evidence on alkaline earth-alkali chloride solutions, as summarized in the work of Sakai *et al*[2].

4 DISCUSSION IN RELATION TO THERMODYNAMIC PROPERTIES

Complex-forming solutions show a characteristic behaviour of the molar heat of mixing ΔH_M as a function of concentration, which is commonly made more conspicuous by plotting the so-called interaction parameter $\lambda_H = \Delta H_M/[c(1 - c)]$ versus concentration. We refer for example to the data of Kleppa and McCarty[16] on complex-forming magnesium-alkali chloride systems: the measured values of λ_H are strongly negative with a deep minimum at $c = \frac{1}{3}$.

Two points need making before we present our results for thermodynamic properties. Firstly, our calculations are carried out at fixed volume rather than constant pressure, and therefore we must refer to an interaction parameter λ_E based on the internal energy $E(c)$ of the solution rather than on its enthalpy. Its definition is

$$\lambda_E = [E(c) - \{(1 - c)\,E(c = 0) + c\,E(c = 1)\}]/[c(1 - c)] \quad (4.1)$$

Secondly, results for energies of mixing based on a charged hard sphere model in the MSA cannot be expected to have quantitative validity, especially in the dichloride-rich range of composition[17]. With this note of caution we report in Figure 3 our results for λ_E in the calcium-alkali chloride systems at $T = 943$ K. There is qualitative agreement with observed behaviours of λ_H insofar as λ_E is small and essentially constant with composition in non-complex-forming solvents, whereas it is of order -10 kcal/mole at low c in complex-forming solvents and shows a strong minimum as a function of concentration. The minimum is located in KCl and RbCl at the concentration where dissociation of complexes starts, and in CsCl at $c = \frac{1}{3}$. Thus, while a strong minimum in the interaction parameter is a trademark of complexing, its position tends to precede the transition from the bound to the dissolved state and is brought to "stoichiometric" composition in cases of high complex stability. Other details of our results for λ_E—in particular, the positive values of the interaction parameter in the complex-free range of composition—are not correct.

Some data on λ_H are available also for calcium-alkali chloride systems from the work of Østvold[18], but they refer to appreciably

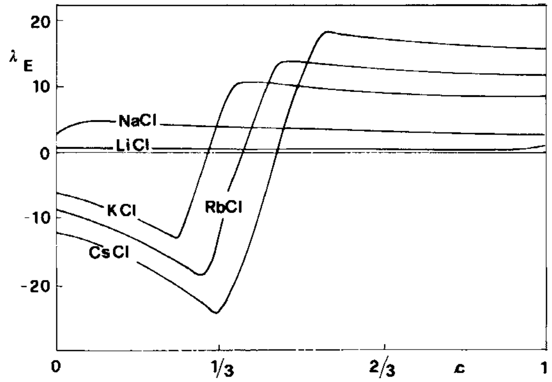

Figure 3 Calculated behaviour of the interaction parameter λ_E (kcal/mole) as a function of concentration c in calcium-alkali chloride systems at $T = 943$ K.

higher temperatures ($T \geq 1083$ K) than our calculations ($T = 943$ K[13]). From the shapes of these data for $\lambda_H(c)$ it appears that complexes are still present at 1083 K in RbCl and CsCl, with $\lambda_H \approx -10$ kcal/mole in the low-c range, whereas they are either absent or present only at low values of c in the KCl solvent. Complex stability depends on temperature in our model primarily through a delicate balance between the increase of the screening length with T and the expected decrease of $|f_c|$ with T. The latter quantity, as we have seen, is dominated by Coulombic interactions and is therefore sensitive to the value of r_{MX}. The best that we can do to make contact with Østvold's data for the $CaCl_2$-KCl system is to estimate the increase in r_{MX} that would be needed over a temperature range of 140 K in order to obtain almost complete dissolution of complexes in this system. This increase turns out to be 0.05 Å approximately. Such changes in temperature and in the value of f_c do not change the results shown in Figures 1 and 3 for RbCl and CsCl in any major qualitative way: dissociation of complexes occurs at somewhat lower values of c and the minimum in λ_E is shallower.

As a final remark we wish to point out that detailed information on complexes and their dissolution process with increasing solute concentration could be obtained by thermodynamic measurements of the excess volume and the heat capacity of the solution. In our ideal-volume calculations the pressure is found to increase steadily with c in the range of concentration where complexes are stable and to decrease rapidly to an essentially zero value across the transition to the complex-free range. We infer that the excess volume should correspondingly be strongly positive in the former range and essentially zero in the latter, with a rapid variation across the transition. For what concerns the heat capacity as a function of composition, we find an essentially linear behaviour between the values for the pure components of the solution except in the transition region, which is marked by a peak in the heat capacity. In arriving at this qualitative prediction account has been taken of the dependence of f_c on temperature that we have commented on above.

Acknowledgements

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13. This is the temperature of the Raman scattering experiments of Sakai *et al.* on $CaCl_2$-$2KCl$ (Ref. 2), to which we refer for refining our assessment of the binding free energy f_c as explained in the text. We note, however, that at this temperature the calcium-alkali halide solutions are liquid only over a limited range of composition. The effect of an increase in temperature is discussed in Section 4, as needed to make contact with thermodynamic data covering the full range of composition in the liquid at 1083 K and above.
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Appendix Expressions of the excess free energies F_{hs} and F_c.

We report here the detailed expressions for the hard-sphere and Coulombic contributions to the excess free energy of our four-component mixture of charged hard spheres, as evaluated in the MSA. The hard-sphere contribution F_{hs} is obtained by integration of the virial pressure in a fluid of neutral hard spheres[14],

$$F_{hs} = \frac{6}{\pi} v k_B T \left[\frac{3\xi_1\xi_2}{\Delta} + \frac{3\xi_2^3}{\xi_3\Delta} + \frac{3\xi_2^3}{\xi_3^2} \ln \Delta - \xi_0 \ln \Delta \right] \qquad \text{(A.1)}$$

where

$$\xi_n = \frac{\pi}{6v} \sum_{\alpha} c_\alpha \sigma_\alpha^n \qquad \text{(A.2)}$$

and $\Delta = 1 - \xi_3$. The suffix α labels the various species, in molar fraction c_α.

The Coulombic contribution F_c is taken from the work of Blum and Høye[8]. Its expression, from integration of the excess Coulombic energy, is

$$F_c = vk_BT\frac{\gamma^3}{3\pi} - e^2\gamma\sum_\alpha \frac{c_\alpha Z_\alpha^2}{1+\gamma\sigma_\alpha} - \frac{\pi v e^2}{2\Delta}\Omega P_n^2 \tag{A.3}$$

Here, Z_α and σ_α are the valence and the diameter of the α species and

$$\Omega = 1 + \frac{\pi}{2v\Delta}\sum_\alpha \frac{c_\alpha \sigma_\alpha^3}{1+\gamma\sigma_\alpha} \tag{A.4}$$

$$P_n = \frac{1}{v\Omega}\sum_\alpha \frac{c_\alpha Z_\alpha \sigma_\alpha}{1+\gamma\sigma_\alpha} \tag{A.5}$$

Finally, the inverse length γ in these expressions is to be determined by solving the equation

$$\gamma = \tfrac{1}{2}k_0\sqrt{\sum_\alpha c_\alpha\left(Z_\alpha - \frac{\pi}{2\Delta}\sigma_\alpha^2 P_n\right)^2\Big/(1+\gamma\sigma_\alpha)^2} \tag{A.6}$$

with $k_0 = (4\pi e^2/vk_BT)^{1/2}$.