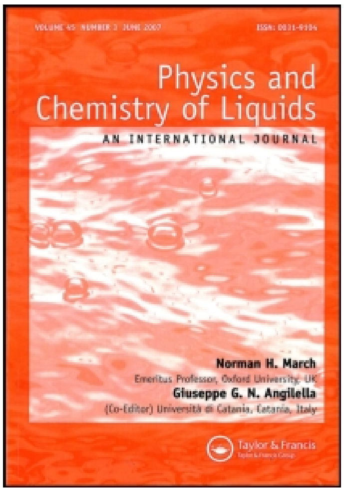

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Co-ordination of heterovalent cation lmpurities in molten salts

W. Andreoni[a]; M. Rovere[b]; M. P. Tosi[cd]
[a] Département de Physique de la Matière Condensée, Université de Genève, Switzerland [b] Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy [c] International Centre for Theoretical Physics, Trieste, Italy [d] GNSM-CNR, lstituto di Fisica Teorica dell'Università, Trieste, Italy

To cite this Article Andreoni, W. , Rovere, M. and Tosi, M. P.(1982) 'Co-ordination of heterovalent cation lmpurities in molten salts', Physics and Chemistry of Liquids, 12: 1, 37 — 44
To link to this Article: DOI: 10.1080/00319108208084540
URL: http://dx.doi.org/10.1080/00319108208084540

Phys. Chem. Liq., 1982, Vol. 12, pp. 37–44
0031-9104/82/1201-0037$06.50/0

Co-ordination of Heterovalent Cation Impurities in Molten Salts

W. ANDREONI
Département de Physique de la Matière Condensée, Université de Genève, Switzerland

M. ROVERE
Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy

and

M. P. TOSI
International Centre for Theoretical Physics, Trieste, Italy
and
GNSM-CNR, Istituto di Fisica Teorica dell'Università, Trieste, Italy

(*Received February 17, 1982*)

The local liquid structure around heterovalent cation impurities in molten alkali chlorides is discussed in relation to spectroscopic data on solutions of transition metals ions. A tightly packed, low co-ordination shell is shown to be favoured by Coulomb ionic interactions for physically reasonable values of the size of the impurity. A competition between these forces and "crystal field" interactions favouring octahedral co-ordination is thus to be expected for many transition metal ions, as suggested by Gruen and McBeth. The transition observed for some transition metal ions from higher to lower co-ordination with increasing temperature is attributed primarily to entropy differences, that are roughly estimated in a solid-like model.

I INTRODUCTION

The optical spectra of transition-metal ions dissolved in molten salts reflect the local structure of the surrounding liquid through the induced splitting of the *d*-electron energy levels. Many cases have been examined[1] using a liquid LiCl-KCl mixture of eutectic composition as the solvent and the data have been interpreted in terms of the formation of chlorocomplexes. For several divalent ions (Ni^{2+}, Cu^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+} and Mn^{2+}) tetrahedral-type co-ordination is the only one observed, with an appreciable distortion from ideal tetrahedral symmetry for the three former ions. Trivalent ions form six-fold co-ordinated chlorocomplexes more readily, a clear example being Cr^{3+} for which only octahedral-type co-ordination is observed. Of special interest are the cases of Ti^{3+}, V^{3+} and V^{2+}, for which the spectroscopic data show a transition with increasing temperature from an octahedral configuration to a situation of equilibrium between octahedral and distorted tetrahedral complexes in co-existence. Typically such a transition is identified through a red shift of the absorption band accompanied by an increase of spectral intensity.

The octahedral configuration is favoured by "crystal field" interactions for all these transition-metal ions with the exception of Mn^{2+}, whose ground state S is not split in a crystal field. Gruen and McBeth[1] have consequently proposed that the crystal field term is counterbalanced by electrostatic terms favouring tetrahedral co-ordination, and have estimated their magnitude for the two valence states by an analysis of the data on V^{2+} and V^{3+}.

Rather detailed information on the structure of pure molten salts has become available in recent years through the use of neutron diffraction techniques,[2] supplemented by computer simulation studies[3] of ionic models for these liquids. Simple theoretical models have also been developed, which give a reasonable semiquantitative account[4] of these structural data. This has encouraged us to examine in this paper the co-ordination of heterovalent cation impurities in molten chlorides. The qualitative questions that we discuss in Section II in an electrostatic model for the interionic forces are the effects of the size and of the valence state of the impurity, the effect of temperature and the differences between a pure chloride solvent and the LiCl-KCl solvent. Our results show indeed a tendency of the impurity to form a low co-ordination, tightly packed shell of first neighbours, in the absence of crystal field effects. We then give in Section III a rough estimate of the entropy difference between octahedral and tetrahedral co-ordination on a solid-like model, to make connection with the observed shift of co-ordination of transition metal ions with increasing temperature.

II LOCAL LIQUID STRUCTURE AROUND HETEROVALENT CATION

The calculations of liquid structure reported in this section are based on a charged-hard-spheres model for the molten salt. Our main concern is the pair correlation function $g_i(r)$ which gives the radial distribution of chlorine ions around the impurity ion, to be contrasted with the pair correlation functions $g_K(r)$ and $g_{Li}(r)$ between the host cations and the chlorine ions in the LiCl-KCl solvent at eutectic composition. Calculations are also carried out for a pure KCl and a pure LiCl solvent. These distribution functions are evaluated in the mean spherical approximation (MSA) using its analytic solution[5] for the set of direct correlation functions in the liquid at vanishingly small concentration of heterovalent impurities.

The parameters of the model at a given temperature and density are the ionic valences and the ionic hard sphere diameters. Integer values are attributed to the valences, i.e. no allowance is made for core polarization effects in accord with previous work on short-range order in molten salts. The hard-sphere diameters for the ions of the solvent are taken from previous results[4] on the structure of pure molten salts. These diameters are $\sigma_{Cl^-} = 2.80$ Å, $\sigma_{K^+} = 2.58$ Å and $\sigma_{Li^+} = 1.44$ Å at freezing, with a weak dependence on temperature. The hard-sphere diameter of the impurity is varied within reasonable limits to examine the effect of this physical parameter on the surrounding liquid structure.

The radial distribution function $g_i(r)$ for a divalent impurity in LiCl-KCl at 600°C is reported in Figure 1 and compared with the corresponding $g_K(r)$ and $g_{Li}(r)$. The diameter of the impurity has been taken as $\sigma_i = 1.9$ Å, a rather large value for transition-metal ions since the ratio of Pauling radii for these ions and for K^+ is in the range $0.5 \div 0.6$. The impurity clearly builds up in our model a tight shell of first neighbour chlorine ions, although our MSA results are of only qualitative value as shown by the negative values taken by the calculated $g_i(r)$ outside this shell. The Li^+ ion, having a small size, it also indicated to be in a rather tightly packed configuration. This result is in accord with computer simulation results[6] on the LiCl-KCl mixture.

From these results we build an average co-ordination number of first neighbour chlorine ions for each cation by integrating the function $4\pi r^2 g(r)$ up to its first minimum. This procedure should roughly correct in this integrated property for the inaccuracies in $g_i(r)$ that we have pointed out above. The results as functions of temperature for divalent and trivalent impurities of various sizes are reported in Figure 2. The co-ordination numbers for the host cations are $n_{K^+} \simeq 5$ and $n_{Li^+} \simeq 3.5$, gently falling with increasing temperature. These are in essential accord with the simulation results of Caccamo and Dixon,[6] who also report only small effects of temperature on the structure of the mixture between 627°K and 1045°K. The co-ordination numbers for divalent impurities fall between the above values for the host cations and become of the order of 4 for impurity radii in the range appropriate to transition-metal ions. Slightly higher co-ordination numbers, of the order of $4.5 \div 5$ are indicated for trivalent impurities. The effect of temperature on these co-ordination numbers is quite small.

On comparing the above results with similar results for the pure LiCl and KCl components, one notices that the LiCl component in the mixture

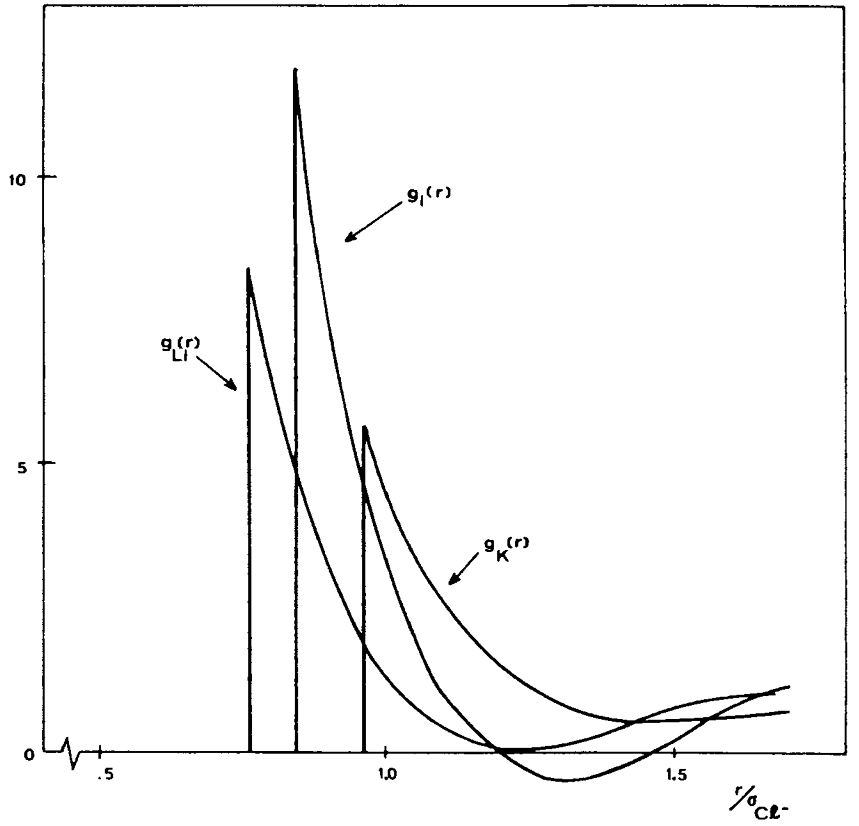

FIGURE 1 Radial distribution functions $g_i(r)$, $g_{Li}(r)$ and $g_K(r)$ in the eutectic LiCl-KCl mixture at 600°C. The diameter of the impurity has been chosen as $\sigma_i = 1.9$ Å.

introduces some additional disorder and tends to favour lower impurity co-ordinations relatively to pure KCl. A further lowering of impurity co-ordination is indicated for pure LiCl as a solvent.

Only a qualitative connection is of course possible between the foregoing results and the spectroscopic evidence on solutions of transition metal ions. The main qualitative point from our calculations is that the heterovalent cation gains electrostatic free energy through a tightening of its co-ordination shell rather than through an increase in its co-ordination. Indeed a tight co-ordination shell implies low co-ordination, on account of the size of the chlorine ions which constitute this shell. In the case of transition-metal ions, as we noted in the introduction, this tendency to low co-ordination is opposed by the crystal field interactions favouring six-fold co-ordination. The equilibrium situation is thus determined by a delicate balance between

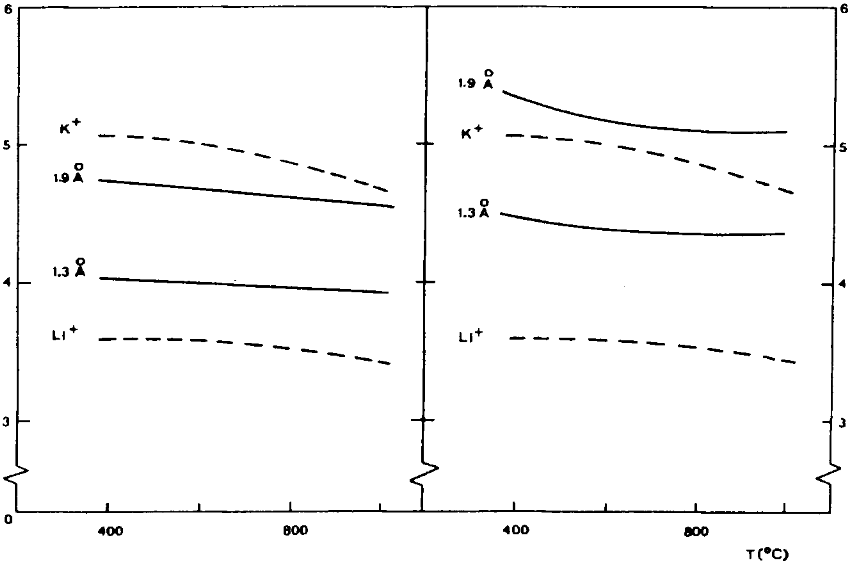

FIGURE 2 Co-ordination numbers vs. temperature in the eutectic LiCl-KCl mixture for divalent (left) and trivalent (right) impurities of indicated diameters. The broken lines are the co-ordination numbers for K^+ and Li^+ ions.

these two gross effects, necessarily involving more subtle effects such as some covalent bonding.

It is also interesting to note that Gruen and McBeth[1] have estimated from the data on V^{2+} and V^{3+} that the electrostatic free energy gain in lowering the co-ordination is appreciably larger for the divalent ion than for the trivalent ion, as necessary to balance a larger crystal field term for the former ion. Our results in Figure 2, which suggest a lower average co-ordination for divalent impurities, are in qualitative accord with their conclusion.

III ENTROPY DIFFERENCE BETWEEN OCTAHEDRAL AND TETRAHEDRAL CO-ORDINATION

The calculations that we have reported above refer to the overall equilibrium state of the liquid in the absence of crystal field effects and do not allow us to assess the free energy difference between alternative co-ordination states of the impurity. The observation that some transition metal impurities have a preferred octahedral co-ordination at low temperature but attain a mixed configuration at high temperatures suggests that entropy differences between the two co-ordinations may be important. We estimate below this effect in a viewpoint in which we try to fit the impurity into the solvent structure and assimilate the latter, at least as far as short-range order is concerned, to a solid-like structure.

In this viewpoint we visualize the spacial arrangement of the host ions in the liquid as being on average similar to that of a NaCl-type structure and identify the octahedral site and the tetrahedral site for the transition metal ion as the substitutional (0, 0, 0) site and the interstitial $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ site, respectively. In the latter configuration a strong gain of Madelung energy can occur through a strong inward relaxation of the four neighbouring chlorine ions and a strong outward relaxation of the four neighbouring alkali ions. This relaxation is favoured by small sizes of the interstitial ion and of the host alkali ions, as is the case for transition-metal ions and for Li^+ ions. In this view a distortion of the tetrahedral configuration would be described as a shift of the mean position of the transition-metal ion away from the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ site and towards the (0, 0, 0) site, the driving force being due to the crystal field stabilization energy for octahedral co-ordination.

The entropy difference between the two ideal co-ordination states arises both from configurational effects and from "vibrational" effects. Concerning the former we notice that the number of interstitial sites is double that of substitutional sites and that the interstitial impurity is accompanied by an additional alkali-ion vacancy. Depending on whether this extra vacancy is distributed on the 4 first neighbour sites or on the 24 second-neighbour sites, we thus have

$$\Delta S_{\mathrm{conf}}/k_B \simeq \ln 8 \div \ln 48 \tag{1}$$

in favour of the interstitial site. The vibrational contribution associated with this extra vacancy can be roughly estimated from data on the formation of Schottky defects in alkali halide crystals[7]

$$\Delta S_{\mathrm{vib}}^{\mathrm{vac}}/k_B \simeq 1.7, \tag{2}$$

while the corresponding contribution associated with vibrations of the first neighbours of the impurity can be estimated by an Einstein model[8] as

$$\Delta S_{\mathrm{vib}}^{\mathrm{imp}}/k_B \simeq -\tfrac{1}{2}\left[4 \ln\left(\frac{k_i}{k_0/\sqrt{3}}\right) - 6 \ln\left(\frac{k_s}{k_0/2}\right)\right]. \tag{3}$$

Here k_i, k_s and k_0 are force constants for first neighbours of an interstitial impurity, a substitutional impurity and a host cation, respectively. We estimate $k_s \sim k_i\sqrt{3}/2 \sim Zk_0$, where Z is the impurity valence. Therefore,

$$\Delta S_{\mathrm{vib}}^{\mathrm{imp}}/k_B \simeq \ln(2Z). \tag{4}$$

The total estimated entropy difference in favour of an interstitial configuration thus is

$$\Delta S \simeq (5 \div 8)k_B \tag{5}$$

with only a weak dependence on the valence of the impurity.

From the results of Gruen and McBeth[1] on V^{2+} and V^{3+}, if we assume a drop by at least a factor of ten in the ratio of tetrahedral-to-octahedral configurations from 1000°K to 400°C and attribute such a drop exclusively to an entropy factor, we get $\Delta S \sim (8 \div 10)k_B$, in fair accord with the above theoretical estimate.

IV SUMMARY AND CONCLUDING REMARKS

We have shown that heterovalent cation impurities with sizes typical of transition-metal ions in molten alkali chlorides are driven by the electrostatic free energy to an essentially fourfold co-ordination in a divalent ion case and to a somewhat higher average co-ordination in the trivalent ion case. An entropy difference between alternative co-ordination states, in the presence of crystal field interactions, is believed to be an important factor in determining their equilibrium at high temperatures. Refinements of the present crude model for the liquid structure would allow a closer contact with the spectroscopic evidence through calculations of shifts and widths of the absorption bands. We believe that also more accurate experimental data are required to determine quantitatively the interbalance between tetrahedral and octahedral complexes.

The occurrence of tetrahedral co-ordination for the divalent 3*d*-transition metal impurities with chlorine ions in molten alkali chlorides is of particular interest because such tetrahedral complexes are extremely rare in binary crystalline phases. Such divalent impurities in crystalline alkali halides have been obtained in a few cases[9] and seem to enter substitutionally (co-ordination number 6), apart from the exceptional case of Co^{2+} which enters interstitially[10] (co-ordination number 4) in both NaCl and KCl. It must be noticed however that in general an impurity entering a crystal is not as free as in liquids in choosing its co-ordination shell. When 3*d*-transition metal atoms co-ordinate to chlorine atoms to form crystalline dichlorides, the co-ordination is invariably octahedral ($CdCl_2$ or CdI_2 structures). In these cases obviously the interactions between transition metal ions are expected to be relevant, in contrast to the case of dilute transition-metal solutions. We also notice a decrease of co-ordination number for the 3*d*-transition metal ions in molten alkali fluorides[1] (co-ordination number 6) with respect to the case of transition-metal difluorides (co-ordination number 8). A systematic comparison between measurements on the solid and the liquid phase would also be very useful.

Acknowledgements

One of us (W.A.) wishes to thank J. C. Phillips, A. Baldereschi, L. Pietronero and M. Parrinello for stimulating and useful discussions.

References

1. D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963), and references given therein; D. M. Gruen, *Fused Salts*, Ed. B. Sundheim (McGraw-Hill, New York 1964), Ch. 5.
2. F. G. Edwards, J. E. Enderby, R. A. Rowe and D. I. Page, *J. Phys.*, C **8**, 3483 (1975); E. Mitchell, P. F. J. Poncet and R. J. Stewart, *Phil. Mag.*, **34**, 721 (1976).
3. See, e.g., M. J. L. Sangster and M. Dixon, *Adv. Phys.*, **25**, 247 (1976).
4. M. C. Abramo, C. Caccamo, G. Pizzimenti, M. Parrinello and M. P. Tosi, *J. Chem. Phys.*, **68**, 2889 (1978); M. Parrinello and M. P. Tosi, *Riv. Nuovo Cimento*, **2**, No. 6 (1979).
5. L. Blum and J. S. Høje, *J. Phys. Chem.*, **81**, 1311 (1977).
6. C. Caccamo and M. Dixon, *J. Phys.*, **C13**, 1887 (1980).
7. A. B. Lidiard, *Handb. Phys.*, **20**, 246 (Springer-Verlag, Berlin 1957).
8. G. H. Vineyard and G. J. Dienes, *Phys. Rev.*, **93**, 265 (1954).
9. S. Hirako and R. Onaka, *J. Phys. Soc. Japan*, **47**, 1019 (1979); T. Iri, S. Hirako and K. Kambe, *J. Phys. Soc. Japan*, **46**, 106 (1979).
10. T. Nasu, *Phys. Stat. Sol.*, (*b*) **70**, 97 (1975).