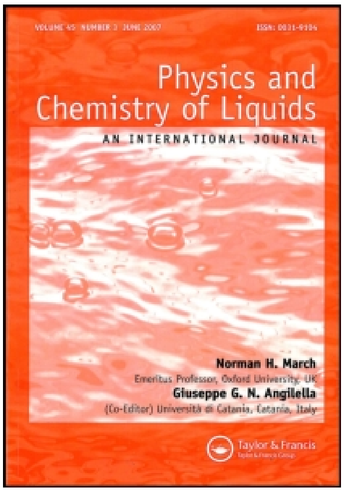
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

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

Coordination Chemistry and Ionic Solvation in Divalent Metal Halide Aqueous Solutions

P. V. Giaquinta[ab]; M. P. Tosi[ac]; N. H. March[a]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] Istituto di Fisica Teorica, University of Messina, Messina, Italy [c] International Centre for Theoretical Physics and the University, Trieste, Italy

To cite this Article Giaquinta, P. V. , Tosi, M. P. and March, N. H.(1983) 'Coordination Chemistry and Ionic Solvation in Divalent Metal Halide Aqueous Solutions', Physics and Chemistry of Liquids, 13: 1, 1 — 24

To link to this Article: DOI: 10.1080/00319108308080759

URL: http://dx.doi.org/10.1080/00319108308080759

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1983, Vol. 13, pp. 1–24
0031-9104/83/1301-0001$18.50/0

Review Article

Coordination Chemistry and Ionic Solvation in Divalent Metal Halide Aqueous Solutions

P. V. GIAQUINTA†, M. P. TOSI‡ and N. H. MARCH
Theoretical Chemistry Department, University of Oxford,
1 South Parks Rd., Oxford OX1 3TG, England

(*Received February 4, 1983*)

CONTENTS

1. Introduction
2. Coordination chemistry of metal ions
    2.1 d^0-cations
    2.2 d^{10}-cations
    2.3 d^n-cations
    2.4 Distortion of octahedral complexes: case of Cu^{2+}.
    2.5 Tetrahedral stereochemistry of d^n-cations.
3. Crystal structures of hydrated salts.
    3.1 Alkaline-earth halides
    3.2 Transition metal halides
    3.3 d^{10}-ion halides
    3.4 Crystal structure of anhydrous $ZnCl_2$.
4. Local coordination of metal ions in water.
    4.1 $CaCl_2$
    4.2 $NiCl_2$
    4.3 $CuCl_2$
    4.4 Zinc halides in water
    4.4.1 Structural and optical studies
    4.5 Cadmium and mercury halides in water.
5. Summary and conclusion

---

† Permanent address: Istituto di Fisica Teorica, University of Messina, Messina, Italy.

‡ On leave from the International Centre for Theoretical Physics and the University, Trieste, Italy.

1 INTRODUCTION

The recent structural investigations of divalent metal halide aqueous solutions, using neutron diffraction studies, have been extensively reviewed.[1,2] Less attention, however, has been given to the chemical effects in such aqueous solutions, an area we have focussed attention on in earlier work.[3,4] In particular, in Ref 3 we pointed out that crystal structure studies have considerable relevance to what goes on locally in aqueous solutions, and we shall again put some emphasis on this topic in the present review (cf. Section 3 below). Secondly, in Ref. 4, we drew attention first to the fact that *X*-ray data also contained intrinsic information related to chemical effects and secondly we pointed out that, while a lot of the available structural data at that time was on static structure, chemical models of structural units could be fruitfully tested by dynamic studies, and in particular by diffusion experiments. Subsequently, dynamical structure has been studied by neutron inelastic scattering,[5] and related to the diffusion experiments discussed above. The diffusion data above was on $NiCl_2$ in aqueous solution: a further example of the value of such data is presented[6] when we discuss zinc halides in aqueous solution. Of course, there is a variety of other data that contributes to the overall picture of divalent metal halide aqueous solutions, optical studies, EXAFS and so on, and we shall at least refer to some examples and give a few of the relevant references.

Because the present review is focussed on chemical effects, we shall not go over the body of (largely) neutron data summarized elsewhere. Rather we turn to a brief review of the coordination chemistry of metal ions immediately below.

2 COORDINATION CHEMISTRY OF METAL IONS

Metal ions exhibit a variety of behaviour in an aqueous environment, as far as their tendency to form purely hydrated or strictly ionic complexes is concerned. In particular, markedly different selective preferences are exhibited for one type or another among the ligands offered to them in solution. In this respect, cations can be divided into three classes: those with a rare-gas electronic configuration (d^0-cations), those with a complete outer d-shell of ten electrons (d^{10}-cations) and the transition metal cations with partially filled d-orbitals (d^n-cations).

2.1 d^0-cations

The physical chemistry of the compounds involving d^0-electrons can be characterized almost exclusively on the basis of the Coulombic interactions which arise between these ions and the oppositely charged ions or oriented dipoles.[7,8] The low ionization potentials of metals, their heats of hydration and dissociation constants, the manifest difficulty to coordinate uncharged ligands with a small dipole moment in a complex: all this clearly does indicate the major role played by electrostatics on the thermodynamical and structural properties of aqueous solutions of d^0-cations.

A way to measure the stability of a hydrated complex ion in solution is through the equilibrium constant K for the reaction

$$M(H_2O)_a + L(H_2O)_b \rightleftharpoons ML(H_2O)_c + (a + b - c)H_2O \qquad (1)$$

where M is any metal ion and L is the appropriate ligand (charges being omitted).

The stability of the complex formed with a given ligand normally increases with the ratio of the charge to the radius (Ze/r_c) of the metal ion. On the other hand, the smaller fluoride ion is preferred to a larger halide ion, and so usually is the stronger dipole of H_2O with respect to ammonia. It is interesting to note that also the anions of the heavy halides find difficulty to compete with the water molecules of the solvent. The d^0-cations are in fact known to react only with fluoride to an appreciable extent and hardly form complexes with other halogen ions even when present in overwhelming excess with respect to the concentration of metal ions in the aqueous solution.

In any case, a large cation will more strongly coordinate anions with, at the same time, a reduction in the solvation of both ions. Such a size effect clearly shows up in the activity coefficient γ of salts of d^0-cations: with large anions such as Cl^-, Br^-, I^-, ClO_4^-, γ decreases with increasing radius of the cation for both alkali and alkaline-earth salts. Even a very simple and still crude electrostatic model can already account for the result of the relative competition between the ligand and the solvent molecules as a function of the metal ion size.

To this end, we next calculate the mutual potential energy U of a model dipole in contact with, and fully oriented by, a cation of radius r_c and charge Ze.[8] The test dipole is formed by one unit of electronic charge at a distance of 1 Å from a unit of protonic charge centred in a molecule of 2 Å diameter, the total dipole moment thus being 4.8 Debye. This is a not unreasonable value for a water molecule, with a permanent dipole moment of ~1.8 Debye, in the intense polarization field generated by the ions. From elementary electrostatics one has

$$U = \left(\frac{1}{r_c + 1.5\ \text{Å}} - \frac{1}{r_c + 0.5\ \text{Å}}\right)\frac{Ze^2}{\varepsilon} = \phi\left(\frac{Ze^2}{\varepsilon}\right) \qquad (2)$$

where ε is the dielectric constant of the solvent. The value of ϕ as a function of the metal ion size, r_c, together with the corresponding values for the

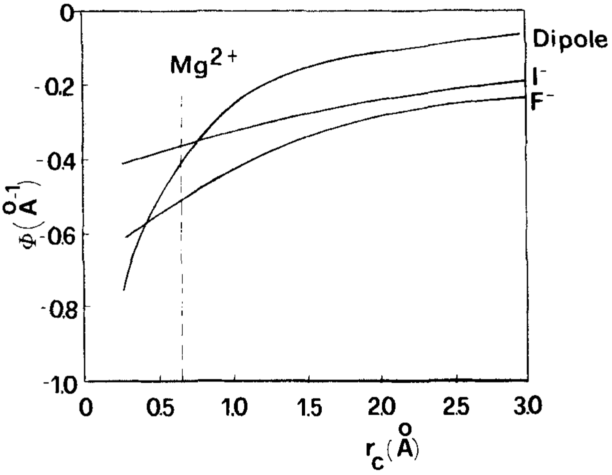


FIGURE 1 Interaction energy ϕ (in units of Ze^2/ε) of a cation of radius r_c with a model dipole and with F^- and I^- ions (with very different ionic radii). The Pauling radius of Mg^{2+} is explicitly indicated by the vertical broken line (Redrawn from J. E. Prue, Ref. 8).

electrostatic interaction of the cation with I^- and F^-, is shown in Figure 1. It turns out, even from this extremely simplified picture of the competition effect between negative ions and water, that small cations will definitely prefer the presence of the solvent dipole molecules, in their first coordination shell, to that of the large halide ions.

2.2 d^{10}-cations

The behaviour of d^{10}-cations in their complex-forming tendencies is quite different from that discussed above. Metal ions like monovalent silver Ag^+ or divalent cadmium Cd^{2+}, give rise to halide complexes of considerable stability, especially in solutions with high stoichiometric ratios in the relative concentration of anions to cations.

In the series of halogen ions, the heavy halides are usually preferred to, say, fluoride as a possible ligand, and the same is generally true for ammonia with respect to the more polar water molecule.

Also the ionic size acts in an opposite sense to that outlined above for d^0-cations: complexes formed with larger ions (both positive and negative) exhibit a greater stability. In this respect it is illuminating to quantify such effects for an isoelectronic series of d^{10}-cations, such as Ag^+, Cd^{2+} and In^{3+}.

Table I records values for the logarithm of the equilibrium constant of the reaction (1) as for the tendency to form halide and ammine complexes in solution.

TABLE I

Stability constants (log K_1) of some d^{10}-cations for halogen and ammine ligands (cf. Ref 7)

Ligand	Ag^+	Cd^{2+}	In^{3+}
F^-	−0.2	0.5	3.8
Cl^-	3.4	1.9	~2
Br^-	4.2	2	1.8
I^-	7	2.3	1.7
NH_3	3.2	2.5	–

It is seen that for low charge metal ions the trend is opposite to that one would expect on the basis of purely electrostatic arguments. On the other hand, the electrostatic character of the "bonds" in the complex progressively emerges when the charge is increased, such an effect being also accompanied by an inferior stability of the ionic associate with a given halide as a ligand. In this respect, fluorine is an exception, the stability of fluoro-complexes increasing in the series with increasing charge of the metal ion.

In order to explain the anomalous behaviour of this class of cations, it is inevitable to advocate the formation of new and more stable covalent bonds within the ionic complex. More than the change in the radius of the metal cation, it will be its tendency to take up electrons together with the facility of the ligand atom to donate electrons (respectively measured by the ionization potential and by the electronegativity of the element) which will more effectively characterize this "covalent" type of interaction.

Of course, it is not obvious how to discriminate the contribution to the free energy coming from this latter characterization of the bonding with respect to the purely electrostatic part which is always present and is gradually enhanced by high values of the charge to radius ratio of the metal ion.

As an example, the sequence of stabilities of Zn^{2+} complexes with halogen ions is the one that electrostatics would predict, while the opposite is the case for cadmium and mercury.[8]

As far as the coordination number and geometry of divalent d^{10}-cations (zinc, cadmium and mercury) are concerned, the principal criterion is essentially dictated by the need to minimize the mutual electrostatic repulsion between the ligands. Such a condition is better achieved with a tetrahedral configuration, on the basis of pure symmetry arguments; this local arrangement of anions around the central metal ion is in fact the most common stereochemical coordination geometry experimentally observed for complexes of Zn^{2+}, Cd^{2+} and Hg^{2+}, with a consequent primary coordination number of four.

If we limit our discussion to undistorted complexes, then the valence-bond description of tetrahedral bonding involves sp^3 hybridization schemes. It goes without saying that the detailed coordination geometry of the metal complex will be further determined by other relevant factors related to the type and size of the ligand, and with the delicate balance between electrostatic and covalent bonding interactions.

As an example, an octahedral coordination of divalent zinc with six water molecules is also firmly established in dilute aqueous solutions.

2.3 d^n-cations

From the above discussion, we may conclude that the local coordination properties of closed-shell divalent cations can be reasonably well understood, at least in a qualitative way, if one takes into account the relative role played by electrostatic and covalent interactions in the ionic associate.

If we now extend the analysis to the complexing properties of the members of the first transition series, which have an unsaturated outer *d*-electron shell, a new effect which is highly relevant comes into play, namely ligand field stabilization.[9,10] It is an established fact that the interaction of halide ions with distant cations from manganese to copper in aqueous solution is known to be weak from a number of thermodynamic and conductance experimental data. Only the fluoride ion interacts to about the same extent as with, say, alkaline-earth cations. The selective preference of d^n-cations towards water molecules or halogen ions is now strongly influenced by the quantum-mechanical splitting of the energetically degenerate five 3*d* orbitals in the isolated ion, induced by the presence of the "external" field produced by the local environment of solvent molecules and ionic species. For example, the field of six ligands disposed octahedrally around a metal cation has the effect of splitting the *d*-orbitals into a doublet (e_g) and a triplet (t_{2g}), the doublet usually being at a higher level (in weak fields)†.

Values of the ligand field stabilization energies (LFSE) in octahedral and tetrahedral environments are shown in Table II.

Now the mechanism is clear: if the *d*-subshell is not complete (as for the transition metal ions) a more stable state is achieved by filling the lowest energy split *d*-levels first. The extra stabilization gained from this ligand field stabilization energy can be quantitatively assessed from spectrophotometric measurements of the spacing of the split *d*-levels.

If the splitting induced by the local field is not so large that more electrons are paired than in the free ion, this energy gain (i.e. the LFSE) is seen to be

---

† In this group, the electron density is greatest close to the ligands, while in the triplet group it is directed between them.

TABLE II

Ligand field stabilization energies in octahedral and tetrahedral environments (weak fields)

First transition series		Number of d-electrons	Octahedral complex	Tetrahedral complex
Sc^{2+}	Fe^{2+}	1, 6	$-2/5\ \Delta_{oct}$	$-3/5\ \Delta_{tetr}$
Ti^{2+}	Co^{2+}	2, 7	$-4/5\ \Delta_{oct}$	$-6/5\ \Delta_{tetr}$
V^{2+}	Ni^{2+}	3, 8	$-6/5\ \Delta_{oct}$	$-4/5\ \Delta_{tetr}$
Cr^{2+}	Cu^{2+}	4, 9	$-3/5\ \Delta_{oct}$	$-2/5\ \Delta_{tetr}$
Mn^{2+}	Zn^{2+}	0, 5, 10	0	0

Notes on Table II:

i) $\Delta_{tetr} \cong 4/9\ \Delta_{oct}$

ii) t_{2g} and e_g levels in an octahedral environment have energies of $-2/5\ \Delta_{oct}$ and $+3/5\ \Delta_{oct}$ respectively, relative to a weighted mean zero, Δ_{oct} being the total energy splitting achieved between the two groups of new levels. On the other hand, in a tetrahedral environment the doublet e level has the lowest energy and the corresponding values for the same ligands are:[10]

$$e = -3/5\ \Delta_{tetr} \cong -4/15\ \Delta_{oct}$$
$$t_2 = +2/5\ \Delta_{tetr} \cong +8/45\ \Delta_{oct}$$

zero for d^5 and d^{10}-cations (divalent manganese and zinc respectively), while it is maximum for nickel with eight d-electrons.

On the other hand, the polarizing power of the cations (as can be estimated from the first two ionization potentials of the free atoms) systematically increases from manganese to copper, then falling abruptly in correspondence to zinc; the opposite trend, even if less pronounced, being found for the ionic radii.

On the basis of such systematic evidence, ligand field stabilization included, it is then possible to understand that the ordered sequence of stability constants for metal complexes of this series (often known as Irving–Williams order) is almost invariably:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}.$$

We finally note that the deviations in the heats of hydration of the divalent transition metal ions from a simple monotonic increase as a function of the increasing radius can be readily explained by the extra stability conferred on the complex ion by the local, octahedral field of the six solvated water molecules.

2.4 Distortion of octahedral complexes: case of Cu^{2+}

As already mentioned, in the presence of an octahedral environment the d-levels of the metal ion split into a t_{2g} triplet and an e_g doublet. The electronic charge (cf earlier footnote) is distributed very differently in the two levels.

If the e_g levels are unevenly filled, some of the ligands will experience a stronger repulsion than others; this will eventually lead to different metal-ligand bond lengths in the complex. On the other hand, inequality in the t_{2g} levels will not sensibly affect the charge distribution around the metal ion.

Thus it follows that, in the presence of relatively weak local fields, there should be no distortion at all for the electronic configurations d^0, d^3, d^5, d^8 and d^{10}, since in each case the charge density is spherically symmetrical. The d^1, d^2, d^6 and d^7 configurations are not expected to give rise to dramatic distortions because the asymmetry affects only the t_{2g} levels. A relevant distortion of the distribution of electronic charge can indeed be predicted for complexes with d^4 and d^9 central cations.[9]

In the case of a d^9-cation (Cu^{2+} say) a proper analysis of the spatial distribution of e_g levels, together with naive symmetry and electrostatic screening arguments, leads to the conclusion that the local coordination geometry around the central ion will be that of a distorted octahedron, in which either four shorter bonds are found coplanar with the metal atom (a so-called 4/2 configuration) or four long bonds are formed in a plane perpendicular to the direction of two shorter collinear bonds (2/4 configuration).

In the solid state, the 4/2 geometry predominates. Thus, in the case of the crystal hydrate $CuCl_2 . 2H_2O$, whose structure in planar projection is illustrated in Figure 2, the local arrangement consists of planar $CuCl_2(H_2O)_2$ units connected through longer Cu–Cl bonds, with anions bridging between the metal atoms.

The charge distortions just discussed are illustrations of the general Jahn–Teller theorem.[9,10]

Finally, it should be mentioned that square planar compounds can be thought of as the limiting case of two z-axis ligands being removed so far away as not to significantly interact with the metal ion.

2.5 Tetrahedral stereochemistry of d^n-cations

Ligand field stabilization effects are much smaller in tetrahedral complexes than in octahedral ones, owing to the very different values of the ligand field splitting. As already mentioned (cf. notes to Table 2) if Δ_{oct} is the splitting for octahedral coordination, the value for tetrahedral coordination is considered to be about $(4/9)\Delta_{oct}$. The former will thus usually dominate the "site preference energy." Only in the case of the Co^{2+} ion the stabilization energy in tetrahedral sites cannot be neglected. In this case, in fact, one has:

$$(\mathrm{LFSE})_{\mathrm{oct.\,complex}} = -\frac{4}{5}\Delta_{\mathrm{oct}}$$

while

$$(\mathrm{LFSE})_{\mathrm{tetr.\,complex}} = -\frac{6}{5}\left(\frac{4}{9}\Delta_{\mathrm{oct}}\right)$$

$$= \frac{2}{3}(\mathrm{LFSE})_{\mathrm{oct.\,complex}}$$

showing the comparable magnitudes of the energies in this example.

3 CRYSTAL STRUCTURES OF HYDRATED SALTS

It is highly relevant to structure in the liquid phase to consider the types of crystal structures to which chemical bonding effects give rise, in hydrated salts. The data presented below is largely taken from the tabulation of Wyckoff.[11]

3.1 Alkaline-earth halides

The following hydrated crystal compounds are reported:

$MgCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 6H_2O$	$SrCl_2 \cdot 6H_2O$	$BaCl_2 \cdot H_2O$
$Br_2 \cdot 6H_2O$	$Br_2 \cdot 6H_2O$	$Br_2 \cdot 6H_2O$	$Br_2 \cdot H_2O$
	$I_2 \cdot 6H_2O$	$I_2 \cdot 6H_2O$	$I_2 \cdot 6H_2O$
		(also $SrCl_2 \cdot 2H_2O$)	(also $BaCl_2 \cdot 2H_2O$)

Hexahydrated magnesium halides are monoclinic with bimolecular cells: Mg atoms are octahedrally surrounded by 6 water molecules at a distance 2.01–2.07 Å. The structure as a whole can be considered as a pseudo-rhombohedral arrangement of these $Mg(H_2O)_6$ groups and halogen atoms somewhat resembling the $CdCl_2$ structure. Each halogen atom has 8 water molecules as neighbours.

Hexahydrated calcium, strontium and barium halides form hexagonal crystals with a type of layer structure; each alkaline-earth atom being surrounded by 9 water molecules (at distances 2.62 or 2.80 Å for $SrCl_2 \cdot 6H_2O$); each halogen has 6 neighbouring water molecules.

3.2 Transition metal halides

The following hydrated crystal compounds are reported: $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, $CoI_2 \cdot 6H_2O$, $NiCl_2 \cdot 4H_2O$ and $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$. We give some details below for selected cases of relevance for our discussion of aqueous solutions in Section 4.

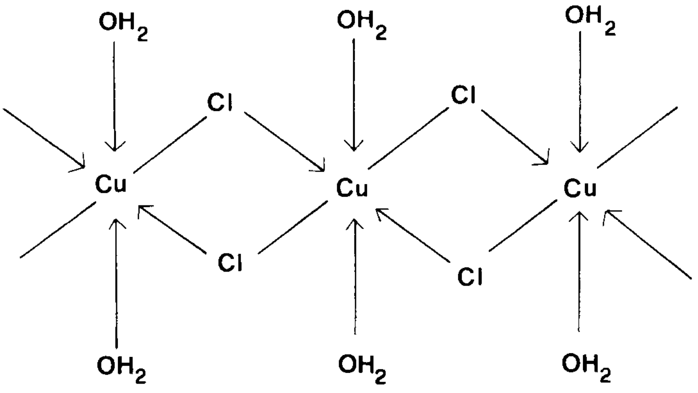


FIGURE 2 Planar projection of the crystal structure of $CuCl_2 \cdot 2H_2O$ (Redrawn from E. Cartmell and G. W. A. Fowles, Ref. 9).

$NiCl_2 \cdot 6H_2O$: this has monoclinic structure with a bimolecular cell; each nickel atom is surrounded by 4 water molecules at the corners of a distorted square with Ni—H_2O = 2.10 Å and by two chlorine atoms (Ni—Cl = 2.38 Å) to form a distorted octahedron. There are thus two kinds of water molecules; the four around the nickel atoms and two others unrelated to the metal atoms†.

$NiCl_2 \cdot 4H_2O$; two kinds of nickel atoms occur in this tetragonal structure, with very different environments. A first type of Ni atom is octahedrally surrounded by 6 water molecules with Ni—H_2O = 2.13 Å. The remaining Ni atoms are not hydrated but have about them 6 octahedrally distributed chlorine atoms with Ni—Cl = 3.31 Å.

$CuCl_2 \cdot 2H_2O$: this has orthorhombic symmetry with a bimolecular unit (see Figure 2). The water molecules and chloride atoms in this structure have a distorted CsCl arrangment. The metal atoms are surrounded by two chloride ions and two water molecules; the copper atoms are the centres of squares (rather than tetrahedra) of these neighbours. The important interatomic distances are: Cu—OH_2 = 1.925 Å, Cu—Cl = 2.275 Å, H_2O—Cl = 3.06 Å, Cl—Cl = 3.72 Å.

3.3 d^{10}-ion halides

No hydrated crystal structures have been reported, as far as we are aware, for halides of zinc, cadmium and mercury. On the other hand metal halide ammoniates exist ($ZnBr_2 \cdot 6NH_3$, $ZnI_2 \cdot 6NH_3$; $CdBr_2 \cdot 6NH_3$, $CdI_2 \cdot 6NH_3$; $HgBr_2 \cdot 2NH_3$, $HgCl_2 \cdot 2NH_3$). The aforementioned compounds that crystal-

---

† The hydrated crystal $CoCl_2 \cdot 6H_2O$ has the same structure with interatomic distances Co—H_2O = 2.12 Å and Co—Cl = 2.43 Å.

lize with six NH_3 molecules have fluorite-like structures such as that assumed for K_2PtCl_6.

The structural arrangement is given by a regular octahedron of ammonia molecules around each metal ion. These octahedra and the halide ions are then distributed as are the calcium and fluorine atoms in CaF_2. Halide ions are equidistant from 12 NH_3 molecules, three from each $M(NH_3)_6$ groups that surround them. Furthermore a large number of more complex crystalline-salt-hydrates containing the group $Zn \cdot 6H_2O^{2+}$ are reported which are not merely metal halide compounds. These are, for instance, $ZnSiF_6 \cdot 6H_2O$, $ZnSnF_6 \cdot 6H_2O$, $ZnTiF_6 \cdot 6H_2O$, $ZnZrF_6 \cdot 6H_2O$. In these compounds, both metallic components are octahedrally surrounded, the silicon say by six fluorine atoms and the zinc by six water molecules. The two sets of octahedra can be thought of as held together by hydrogen bonds between oxygen and fluorine.

3.4 Crystal structure of anhydrous $ZnCl_2$

Recent work indicates that anhydrous $ZnCl_2$ has an orthorhombic unit cell with the Cl^- ions in a hexagonal close-packed sequence (see Figure 3). The Zn^{2+} ions are situated in tetrahedrally distributed holes. The $ZnCl_4^{2-}$

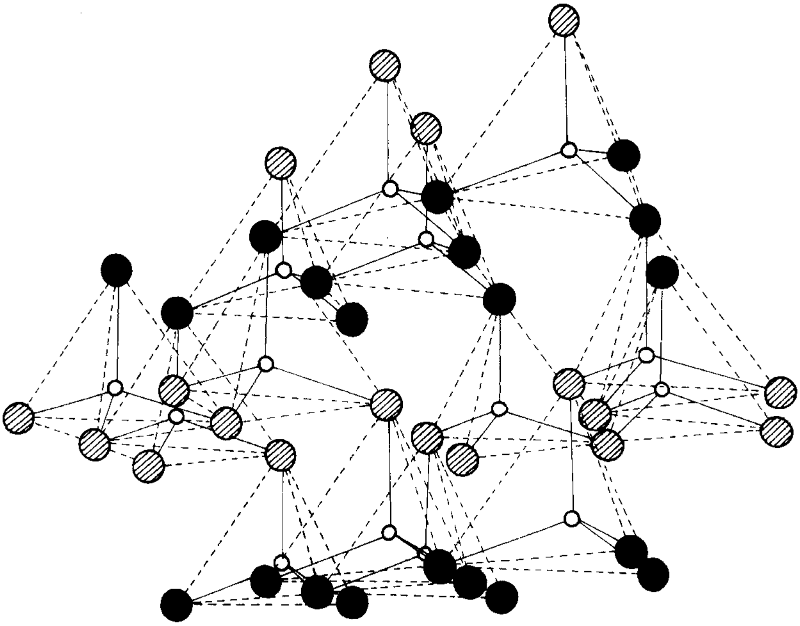


FIGURE 3 The crystal structure of δ-$ZnCl_2$. The smaller circles represent Zn^{2+} ions; the black and shaded circles represent alternate layers of Cl^- ions (Redrawn from Brynestad and H. L. Yakel, Ref. 12).

tetrahedra share corners and not edges or faces in the crystalline state. The possibility of edge or face sharing arises in the liquid and glass. The aforementioned polymorph is referred to as δ-$ZnCl_2$, references being to the work of Brynestad and Yakel.[12] Three other polymorphs are referred to in the literature (see Wyckoff[11]). In particular the so-called γ-form is obtained after crystallization from concentrated solutions. In such a polymorph, the Zn^{2+} ions are all found in tetrahedral sites between alternate sheets of chloride ions, the sandwiches thus formed being held together by van der Waals interactions. Furthermore the Cl^- ions are found in an approximately cubic close packing (HgI_2 type structure). In the remaining two α- and β-polymorphs, the Zn^{2+} ions are found between all chloride sheets and thereby provide a cross-linking effect.

4 LOCAL COORDINATION OF METAL IONS IN WATER

From the above discussion of the main types of coordination that are found in crystal structures, we turn now to our primary interest, the local coordination of metal ions in water. We shall see a correlation between the available data on local coordination and the main features underlined in our previous discussion of coordination chemistry and crystal structure.

4.1 $CaCl_2$

Cummings *et al.*[13] and Hewish *et al.*[14] have carried out neutron diffraction experiments via the technique of isotopic substitution for several concentrations ranging between 1 molal and 4.5 molals. These experiments lead to the following conclusions as to the local environment of Ca^{2+} ions:

i) the first coordination shell of Ca^{2+} ions is formed by water molecules.

ii) two well-defined peaks appear in the weighted radial distribution functions of Ca^{2+}, close to 2.4 Å and 3.0 Å, which can be readily associated with calcium–oxygen and calcium–deuterium distances. Such distances (which agree within experimental error with those derived from X-ray studies) do not vary significantly with concentration.

iii) the number of water molecules to which Ca^{2+} coordinates is strongly concentration dependent, increasing from 6 to 10 as the molality decreases from 4.5 to 1.

iv) the widths of the twin peaks at 2.4 Å and 3.0 Å decrease with increase in concentration, i.e. the first hydration shell gets better defined and more strongly coordinated to Ca^{2+} at higher concentrations.

Such neutron diffraction evidence on the local environment of calcium in water is a clear manifestation of the weakly hydrating nature of Ca^{2+}, whose structural properties in aqueous solutions can then be easily understood on the basis of mainly electrostatic arguments, crucially dependent on the ionic strength, the nature of the counter ion, and possibly the temperature.

Quite recently, incoherent neutron spectroscopy studies have been carried out on a 2.0 molal and 3.0 molal solution of $CaCl_2$ by Hewish *et al.*[15] It turns out that a simple Lorentzian is already able to reproduce quite accurately the experimental data. This means that calcium ions and water molecules are in a so-called "fast-exchange" regime. The same experiment performed on $MgCl_2$ aqueous solutions (with the same molalities) shows that at least two Lorentzians are needed to reproduce the experimental data. The existence of two different diffusion mechanisms inferred from this for water molecules in the solution calls for a more persistent (on the time scale of the experiment) hydration cloud around Mg^{2+}, at variance with the above Ca^{2+} case. Nevertheless, in this latter case, also a two Lorentzian fit has been tried in order to account for possible second hydration shell effects. Water and cations in the Mg^{2+} case are now in a "slow-exchange" regime.

The ability of Mg^{2+} to more tightly coordinate the H_2O molecules with respect to Ca^{2+} has to be related to the smaller radius of the ion (0.65 Å for Mg^{2+} against 0.99 Å for Ca^{2+}) and thus to an increased ratio (charge/radius), which determines a higher dipole–ion interaction strength.

4.2 $NiCl_2$

The local coordination arrangement of Ni^{2+} in water is now fairly well established by neutron diffraction experiments by Enderby *et al.*[1] We shall restrict ourselves here to stressing some differences with respect to Ca^{2+} in water. First of all, the number of hydrated water molecules (6) around each Ni^{2+} ion is, within experimental error, independent of concentration. Furthermore the widths of the first peak for both $g_{\mathrm{NiO}}(r)$ and $g_{\mathrm{NiD}}(r)$ increase with increase in the concentration. Both effects are opposite to those observed in $CaCl_2$ aqueous solutions.

Such different behaviour can be understood on the basis of the quite distinct coordination chemistry of Ni^{2+} vs Ca^{2+}. Ligand field stabilization effects produce a well defined octahedral coordination of 6 water molecules around each Ni^{2+} ion, the "bonding" between Ni^{2+} and H_2O molecules being essentially chemical rather than electrostatic. Moreover, such a strong chemical coordination would be expected to be less "disturbed" at lower concentrations, as is found. Indeed there is both static (neutron diffraction) and dynamic (incoherent quasi-elastic neutron scattering by

Hewish *et al.*[16]) evidence for a gradual building up of a second hydration shell of 12 water molecules (for $3.5\ \text{Å} < r < 5.5\ \text{Å}$) as the concentration is lowered.[1]

Such conclusions on the structural environment of Ni^{2+} in solution are also confirmed by EXAFS measurements.[17] Sandstrom further reports on a possible outer sphere halogen coordination of the cation (3 Cl^- ions at ~3.1 Å) at molar concentrations 2.78 and 3.74 (saturation concentration for aqueous $NiCl_2$ is ~4.1 molar).

The bridging of Ni^{2+} coordination groups is then tentatively suggested by these results to account for the observed higher than stoichiometric average Cl^- coordination of Ni^{2+}.

Finally a neutron diffraction experiment has been performed on a 3.80 molal solution of nickel perchlorate by Newsome *et al.*[18] It is found that the coordination of water molecules around nickel ions is identical with that found in the $NiCl_2$ solution of comparable ionic strength.

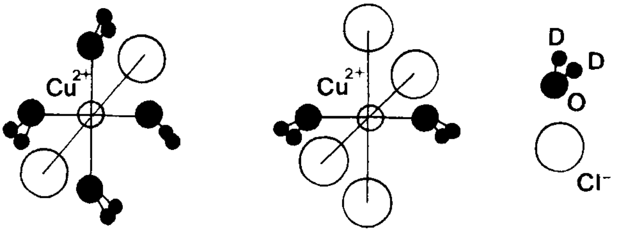
So, at least as far as nickel is concerned, the geometry of ionic hydration seems to be specific to the ion and not influenced by the nature of the counter ion.

4.3 $CuCl_2$

As already discussed in Section 2, the coordination chemistry of copper predicts a 2 + 4 configuration which is essentially due to a distortion of the octahedral arrangement caused by an asymmetrical repulsion between the ligands. Copper thus offers another test case for the possible persistence of chemical effects on the local arrangement around the cation.

A partial answer comes again from neutron diffraction studies carried out by Neilson.[19] At a molal concentration of 4.32 (ca 13 water molecules per metal ion) the neutron weighted distribution function of copper turns out to be significantly different from that of nickel. The two nearest neighbours of Cu^{2+} can be rather unambiguously identified with water molecules with atom positions $r_{CuO} = 2.05$ Å and $r_{CuD} = 2.56$ Å. The identification of next-nearest neighbours is not so clear; two models are consistent with the present level of resolution of the experiment; one with four next-nearest-neighbour Cl^- ions and a second one with two water molecules and two Cl^- ions as next-nearest-neighbours (see Figure 4).

On the basis of the available neutron data, it is not possible to distinguish between these two models. But in any case a 2 + 4 configuration around the Cu^{2+} ion at that (moderately high) concentration is clearly demonstrated. EXAFS measurements for concentrated $CuBr_2$ solutions, made by Fontaine *et al.*[20] and Lagarde *et al.*[21] indicate a local coordination for Cu^{2+} similar to the hydrated salts (fourfold H_2O and twofold Br^- coordination). They



(a) (b)

FIGURE 4 Local coordination models ((a) and (b)) for the Cu^{2+} ion in water, consistent with neutron diffraction data (Redrawn from G.W. Neilson, Ref. 19).

are not consistent with $CuBr_4^{2-}$ anions. Furthermore EXAFS indicate that mean hydration numbers decrease at increasing concentrations. At saturation, the average number of oxygen and bromine atoms around copper is 3.5 ± 0.5 and 3 ± 1 respectively, with distances $r_{CuO} = 1.93$ Å and $r_{CuBr} = 3.3$ Å. There seems to be an indication for the existence of extended structures (anion bridging of coordinated cations) more than isolated groups at high concentration.

4.4 Zinc halides in water

The physical chemistry of zinc halide aqueous solutions is essentially different from both that of transition metals and alkaline-earth halides in water. Thermodynamic, structural and transport properties do considerably distinguish the behaviour of zinc in an aqueous environment from that of other divalent ions with a comparable size.

Let us start from thermodynamics and consider for instance the variation of the activity coefficient γ with concentration as compared with that of other 2 : 1 electrolytes, as discussed by Robinson and Harned[22] (see Figure 5). Alkaline-earth chlorides form a regular series, the activity coefficients diminishing with increasing atomic weight as in the case of alkali-metal chlorides. In a plot of γ vs (molality)$^{1/2}$, the activity coefficients of the latter electrolytes do approach at low concentrations a Debye–Hückel limiting law from above.

The activity coefficients of the chlorides of metals of the transition group do also decrease with increasing atomic number from manganese through cobalt to nickel, the three curves being placed regularly between those of magnesium chloride and strontium chloride. A change occurs with $CuCl_2$ which is found to lie very close to $BaCl_2$, instead of lying above $NiCl_2$. The γ's of a second class of electrolytes are found to approach the Debye–Hückel limit from below. Among these are cadmium halides. These salts are incompletely dissociated even in very dilute solutions and furthermore are

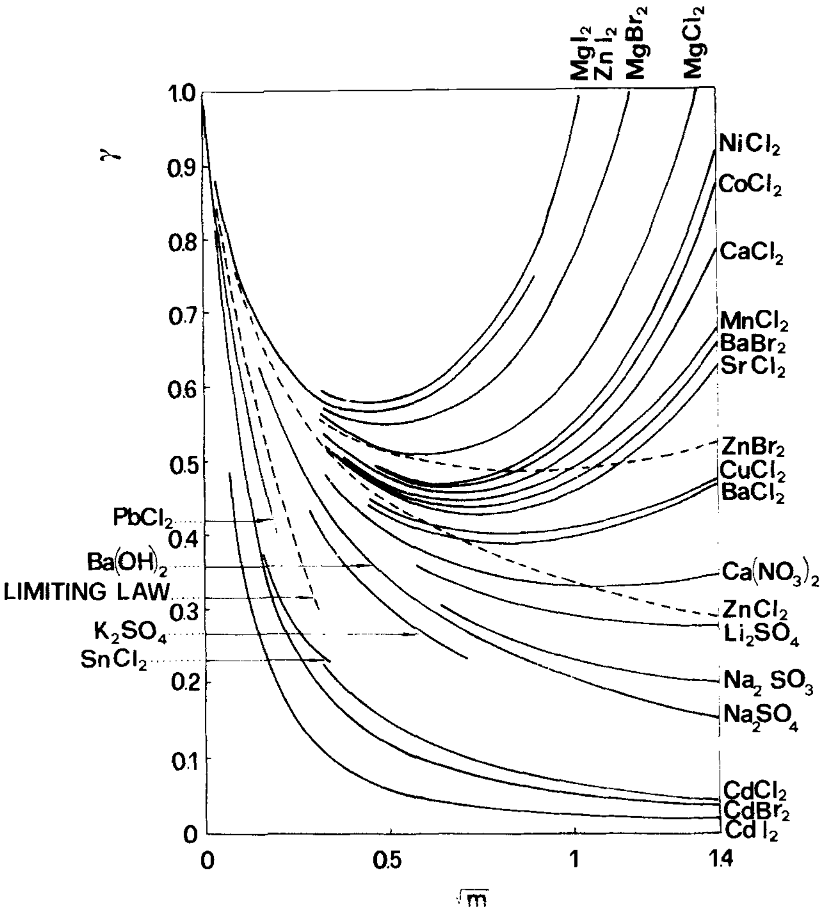


FIGURE 5 Activity coefficient γ of some water solutions as a function of (molality)$^{1/2}$. The Debye-Hückel limiting law is also plotted for comparison (Redrawn from R. A. Robinson and H. S. Harned, Ref. 22).

expected to form complex ions in more concentrated solutions. Ionic association occurs to an extent which makes an estimate of the dissociation constants possible; a value of 0.01 is found for $CdCl_2$, which turns out to be in agreement with that found from conductance measurements.

If we now look at the curves for $ZnCl_2$ and $ZnBr_2$, we find a somewhat peculiar behaviour: in dilute solutions both salts behave as strong electrolytes (γ's above the Debye–Hückel limiting law) but above a concentration of about 0.3 molal the activity coefficient curves begin to descend in such a way as to intersect the curves for many other electrolytes. The departure from the former behaviour points towards the formation of new complex structures in the solution. Zinc iodide does not apparently exhibit such mixed features.

Association is further indicated by the variation of the transport numbers of zinc in aqueous zinc halide solutions, as discussed by Robinson and Stokes.[23] Transport numbers in fact first decrease to zero and then become negative at a concentration of

2.0 molal (27.8 H_2O molecules per Zn) in $ZnCl_2$,
2.7 molal (20.6 H_2O molecules per Zn) in $ZnBr_2$,
3.5 molal (15.7 H_2O molecules per Zn) in ZnI_2.

Such a rapid drop to negative values does not occur in a zinc perchlorate ($Zn(ClO_4)_2$) aqueous solution, which can be taken as typical behaviour for a normal 2:1 electrolyte at higher concentrations ($NiCl_2$ does also behave normally in this respect).

The anomalous behaviour of zinc halide aqueous solutions can only be explained if the metal ion is largely present as a complex negative ion. The concentration at which polyanion complexing of zinc occurs as signalled by the onset of negative transport numbers, increases when going from chlorine to iodine. The same "electrostatically" ordered sequence is found for the relative stability of zinc halogen complexes, as already previously stressed (see Section 2).

4.4.1 Structural and optical studies

No neutron diffraction experiments have been performed so far on Zn-halides in water, to our knowledge. We shall then resort to X-ray studies and Raman spectroscopic experiments to gain some insight into the local structural arrangement of zinc in its aqueous environment. X-ray diffraction studies have been carried out for $ZnCl_2$ in a wide range of concentrations from about 2.6 molal (21.4 water molecules per cation) up to saturation.[24–26] Now the solubility of $ZnCl_2$ in water is so great that the mole ratio of water to zinc chloride can easily be made even smaller than 2:1, also at room temperature. "At such high concentration it becomes a semantic question as to whether the system is called a solution or a molten salt... High viscosity, low electrical conductivity and behaviour in extraction experiments all suggest polymerization in concentrated solution. The great increase in viscosity with increasing concentration cannot be accounted for in terms of simple species .... One therefore suspects, if he assumes at least four coordination for zinc, the existence of some polynuclear species in which chlorines are shared."[25]

Moreover, in order to elucidate the relative behaviour of zinc with respect to chlorines, a number of X-ray,[24] Raman[27–29] and also EXAFS[21,30] studies have been performed with chloride/zinc stoichiometries ranging from 2:1 to 6:1 at moderately low $ZnCl_2$ molarities (1 ÷ 2 M).

The low-angle X-ray scattered intensity of many 2:1 electrolyte solutions shows a characteristic pre-peak which can be interpreted in terms of ion–ion and possible ion–water correlation effects. The intensity of such a pre-peak at a given concentration is found to vary strongly as a function of the solute: it is negligible for $MgCl_2$, while in $CdCl_2$ this low-angle maximum is even higher than the typical water peak at greater k. $NiCl_2$, together with $CuCl_2$, $CoCl_2$ and $FeCl_2$, falls in between these extreme types of behaviour.[16]

As far as the concentration dependence of such a pre-peak is concerned, it is generally found that the height of the peak increases with increasing salt concentration, while its position k_m for many divalent metal ion aqueous solutions varies strictly as a power of the molarity M:[26]

$$k_m = A\,\mathrm{M}^B$$

with different values of the exponent B for the various solutions as reported in Table III.

TABLE III

B values in metal chloride solutions

Co^{2+}	0.47 ± 0.02
Ni^{2+}	0.25 ± 0.01
Zn^{2+}	0.52 ± 0.02
Cd^{2+}	0.35 ± 0.01

As appears clearly, the concentration dependence of the peak position is different for the different solutions. The concentration range of such measurements varied from ~1 molar up to saturation.

Fourier inversion of the scattered X-ray intensity, after corrections for background, polarization, absorption and incoherent scattering, yields an average radial distribution function (RDF) which, in the case of an aqueous $ZnCl_2$ solution, shows at short distances three maxima, at 2.2 Å, 3.0 Å and 3.5–3.7 Å.

From an analysis of the location and area of the primary peak and of the position of the subsequent peaks, it is possible to interpret the experimental data on the basis of a structural model which calls for a tetrahedral coordination of zinc. In fact, the first distance can be readily associated to zinc-chlorine relative separation, in fair agreement with the corresponding value in crystalline zinc chloride. Furthermore the position of the third maximum in the RDF is at about $(8/3)^{1/2} \times 2.2$ Å $= 3.6$ Å as a tetrahedral coordination of chlorines around zinc would require. The second peak can be unambiguously related to oxygen–oxygen and chloride–oxygen interactions characteristic of any aqueous solution containing chloride. But a tetrahedral coordination around Zn^{2+} does not necessarily imply that all the four neighbours are chlorines. In fact it is known that the dissociation constant for $ZnCl_2$ in water by the reaction

$$2ZnCl_2 \rightleftharpoons Zn^{2+} + ZnCl_4^{2-}$$

is ca 0.04 at concentrations of 2 ÷ 3 molal.[31] This means that the predominant species in the solution at such medium concentrations is $ZnCl_2$ with some hydrating waters. There will be, of course, also a number of hydrated bare cations Zn^{2+} and complexes $ZnCl_4^{2-}$. It is then reasonable to analyze the first maximum in terms of zinc-chloride and zinc–water interactions. Under the assumption of a tetrahedral coordination, which can be tested against other possibilities, it turns out that at 2.6 molal (21.4 water molecules per zinc ion), a tetrahedral $ZnCl_2(H_2O)_2$ species can quantitatively account for the scaled X-ray intensity, while, for instance, an octahedral model cannot. When increasing the concentration up to saturation, the average number of water molecules actually coordinated with a zinc ion decreases, while the corresponding number of chlorines increases, the tetrahedral arrangement still preserving its validity in the interpretation of the low-angle features of the X-ray data. At saturation, ca three chlorines and one water molecule seem to form the nearest neighbour environment of zinc. Such a picture turns out to be consistent with EXAFS which give a number of halogens around zinc (in a $ZnBr_2$ aqueous solution) ranging from 2 to 3.5 for concentrations between 1.29 molar and 8.08 molar.[21]

Further, Raman spectra are also in agreement with a tetrahedral structure of the cations as the main local arrangement of the species present in the solution. Indeed in stoichiometric zinc chloride solutions, the most intense Raman band centred at 284 cm^{-1} is asymmetric. However the envelope becomes less asymmetric after the addition of excess chloride. Such behaviour suggests that the species causing the asymmetry in the 284 cm^{-1} band of the zinc chloride solutions do not exist in the presence of excess chloride[27] thus pointing towards an effect of gradual substitution of H_2O molecules in the first coordination shell of Zn^{2+} with chlorines up to the formation of a completely symmetrical $ZnCl_4^{2-}$ complex.

Raman evidence is also given for the presence of sixfold hydrated zinc, $Zn(H_2O)_6^{2+}$, with octahedral coordination. A sixfold coordination of water molecules is to be expected on geometrical grounds if the radius ratio $R_{Zn^{2+}}/R_{H_2O}$ is the major factor determining the stereochemistry of the primary hydration sphere. An octahedral arrangement of H_2O molecules around Zn^{2+} is also found in a number of complex crystalline salt-hydrates. This latter band becomes broader and broader as the concentration is increased and is not observed in spectra of samples containing an excess of chloride ion. The aquozine ion is virtually all converted to the tetrachlorozincate complex in these samples. The interpretation of X-ray data for $ZnCl_2$ solutions with chloride/zinc stoichiometries ranging from 2:1 to 6:1, and with salt molarity of 2.2 ÷ 2.3,[24] consistently indicates that the average number of chlorines occupying primary coordination sites about Zn^{2+} gradually increases from two to four with increasing stoichiometric ratio $[Cl^-]/[Zn^{2+}]$.

Independent EXAFS measurements[30] also support this conclusion. In $CuBr_2 + ZnBr_2$ and in $SrBr_2 + ZnBr_2$ mixed electrolytes, the Sr^{2+} and Cu^{2+} do effectively behave as halogen donors, the average coordination number of bromine ions around zinc rising to 4 as the $[Br^-]/[Zn^{2+}]$ ratio increases.

At this point, we shall briefly summarize work of Easteal *et al.*[6] on chemical effects in diffusion and structure of zinc chloride in aqueous solution. In the absence of neutron data, the existing experimental data for X-ray, Raman scattering, EXAFS and thermodynamic activity studies, all covered to a greater or lesser extent in the present review, was used to build up a consistent model of the structure of $ZnCl_2$ in aqueous solution in the range of molality from 2 up to saturation.

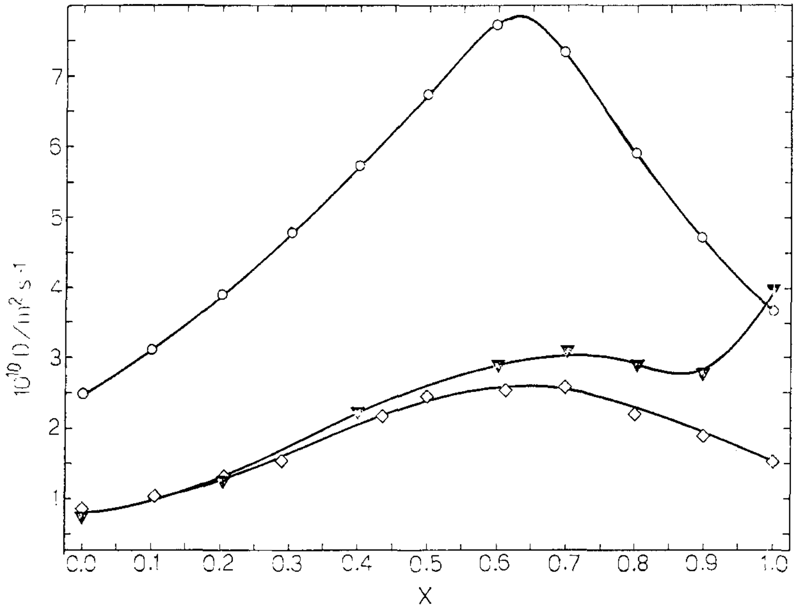


FIGURE 6 Diffusion coefficients at 298.2 K for (1-X)($ZnCl_2$, 4.004 H_2O) + X(LiCl, 4.004 H_2O) mixtures. ○, H_2O ▼ Cl, ◇, Zn.

The structure that emerges is that Zn is tetrahedrally coordinated and that in these coordination complexes the number of Cl ions per Zn ion increases with increasing molality, this implying the existence of extended Zn structures as the saturation concentration is approached.

Relevant evidence in support of these structural models has been obtained by measuring the diffusion constants of Zn, Cl and H_2O when the stoichiometry of the solution is varied by replacing Zn by Li.

Specifically, tracer diffusion coefficients of ^{65}Zn and ^{36}Cl and the self-diffusion coefficient of H_2O, for the pseudobinary mixtures

$$(1 - X)(ZnCl_2, 4.004\,H_2O) + X(LiCl, 4.004\,H_2O)$$

are shown in Figure 6 as functions of mixture composition. It can be seen that for all three diffusion coefficients, D at first increases with Li concentration, the D's of Cl and Zn going together for an appreciable range of Li concentration. It is the water diffusion coefficient that is the most dramatically enhanced.

These data demonstrate clearly that as more Cl ions become available to form complexes with Zn, water molecules are freed to diffuse more rapidly through the solution. The maximum observed in D_{H_2O} with increasing Li concentration is found to occur in the region where approximately 4 Cl ions are available per Zn ion. It is also relevant to note here the gentle minimum in D_{Cl}. This occurs at about 6 Cl ions per Zn ion. After this, Cl ions are freed and D_{Cl} increases.

Thus, in contrast to $NiCl_2$ in aqueous solution, where previous work showed that Ni prefers to form a hydration cloud rather than to associate with Cl ions, the above studies of Easteal *et al* show that in the range between 2 molal and saturation, Zn attracts Cl and prefers Cl, when available, to hydration. The fact that a variety of data supports increasing numbers of Cl ions coordinated to Zn as the concentration of the aqueous solution approaches saturation means that Cl must be shared between Zn ions, leading to a polymeric structure of Zn ions. Such a structure is in agreement with the high viscosity and low conductivity in this regime of molality.

We want finally to comment on the structure of a pure $ZnCl_2$ solution close to saturation. Just on the basis of simple stoichiometric arguments, it is impossible to account for an average coordination of chlorines around zinc greater than two, if sharing of chlorines between zinc atoms does not occur. This bridging effect gives rise to a kind of extended structure rather than to isolated complexes $ZnCl_4^{2-}$ if we assume that all the zinc ions are equivalent.[25] The existence of such polynuclear aggregates gives rise in the Raman spectra of aqueous solutions of $ZnCl_2$ more concentrated than 10 molar to bands characteristic of the melt and of the solid.[27] The intensity of such bands is enhanced by further increase of the concentration up to saturation.

4.5 Cadmium and mercury halides in water

The behaviour of aqueous solutions of cadmium and mercury halides resembles that of the zinc halides, showing again the tetrahedral coordination associated with a d^{10} electronic configuration.

An X-ray diffraction study of aqueous solutions of CdI_2 both in defect and in excess of iodine with respect to the stoichiometric value 2:1, has been carried out together with a Raman spectroscopic investigation.[32] First of all, in a cadmium perchlorate solution, only solvated cadmium ions are reported with six water molecules forming the first hydration shell. In the solution with a ratio $[I^-]/[Cd^{2+}] \simeq 0.73$ and $[H_2O]/[Cd^{2+}] \simeq 46.11$, sixfold solvated cadmium ions and fivefold hydrated $CdI^+(H_2O)_5$ complexes are reported as the main species.

Finally, in the iodine rich limit, $[I^-]/[Cd^{2+}] \simeq 5.07$ and $[H_2O]/[Cd^{2+}] \simeq 13.62$, only the CdI_4^{2-} complex is formed, as it is also clearly seen from the existence in the Raman spectrum of four peaks over the range $< 200\ \mathrm{cm}^{-1}$ which can be attributed to the four characteristic vibration frequencies of a symmetrical tetrahedral complex (T_d symmetry). A number of X-ray diffraction studies has also been carried out to investigate the structure of the mercury halide complexes in aqueous solution.[33,34] For concentrated mercury (II) chloride solutions ($c_{Hg} \gtrsim 1$ M), containing a large excess of chloride (mol ratio Cl/Hg $\simeq 4.5$), a consistent analysis of the experimental data can be based on the dominant presence as a species of a tetrahedral $HgCl_4^{2-}$ complex. Moreover, for solutions with Cl/Hg mol ratios $\simeq 3$ and $c_{Hg} \gtrsim 0.5$ M it was found that a polynuclear, extended structure is formed in the solution, with double chlorine bridges between the mercury atoms.

Again in $HgBr_2$ and HgI_2 concentrated solutions with mol ratio X/Hg $\simeq 3.4$, a tetrahedral coordination of mercury by four halogen ions accounts in a reasonable way for most of the scattered X-ray intensity, which nevertheless seems also to be consistent in the latter two cases with the formation of mononuclear HgX_3^- negative ions when the X/Hg mol ratio is reduced below $\simeq 4.0$. No sharing of X atoms is found for mercury bromide and iodide solutions, in contrast to what is found in the chloride case. The availability of enough halogen ions in the solution allows the formation of isolated complexes.

Finally let us note that results from Raman spectroscopic investigations support a regular tetrahedral structure for the HgX_4^{2-} complexes in solution.[35,36]

5 SUMMARY AND CONCLUSION

It is remarkable to us what a useful local picture of structure in the divalent metal halide aqueous solutions considered in this review can be got from arguments drawn largely from coordination chemistry. That is not, of course, to deny the importance of rather precise factual information that is now forthcoming, especially from diffraction studies. Nor is it to be claimed that the chemical picture can lead to decisive predictions of itself, as there is often a delicate balance between competing effects in determining the precise form of the local structure. Nevertheless, in spite of these reservations, the chemical bonding arguments are extremely helpful in understanding the overall pattern, and certainly also for interpreting the quite different behaviour of, say, zinc halides, from nickel chloride.

It is clear, both from the work we have done ourselves in collaboration with the diffusion research unit at ANU, Canberra, and more recently from the dynamical structure studies made by neutron inelastic scattering, that to get a fuller picture there will be increasing interest in the dynamics, the relevant time scales over which complexes exist, and so on.

Clearly, computer simulation experiments are already beginning to play a role in this field, and though it is, we feel certain, going to be very important to reflect the local chemistry in the force fields used in such computer experiments, these directions of progress are obviously important directions for future work.

Acknowledgement

One of us (NHM) wishes to acknowledge the award of a grant from the Nuffield Foundation which made it possible for P.V.G. to join the other two authors for a period together in Oxford. During this time the present article was largely completed.

One of us (MPT) acknowledges partial support by the Consiglio Nazionale delle Ricerche, under an international collaboration scheme with the British Council, and by the Ministero della Pubblica Istruzione, as well as the award of a Senior Visiting Fellowship from the SERC, UK.

We also want to thank Dr. R. Mills, the Head of the Diffusion Research Unit (DRU) at ANU, Canberra, for vital collaboration with us in this area, and for enabling us to collaborate fruitfully with other members of the DRU, Canberra. Furthermore, Dr. Mills has generously made available to us the results of unpublished work, which have certainly influenced the views expressed in this review. That, of course, in no way commits Dr. Mills and his colleagues: the point of view developed in the article must be the responsibility of the three authors alone.

References

1. J. E. Enderby and G. W. Neilson, *Rep. Progr. Phys.*, **44**, 593 (1981).
2. J. E. Enderby, *J. Phys.*, **C15**, 4609 (1982).
3. N. H. March and M. P. Tosi, *Phys. Lett.*, **50A**, 224 (1974).

4. R. Mills, N. H. March, P. V. Giaquinta, M. Parrinello and M. P. Tosi, *Chem. Phys.*, **26**, 237 (1977).
5. N. A. Hewish, J. E. Enderby and W. S. Howells, *Phys. Rev. Lett.*, **48**, 756 (1982).
6. A. Easteal, P. V. Giaquinta, N. H. March and M. P. Tosi, *Chem. Phys.* (in press).
7. G. Schwarzenbach, *Pure and Appl. Chem.*, **24**, 307 (1970).
8. J. E. Prue, "Ionic Equilibria", "*International Encyclopedia of Physical Chemistry and Chemical Physics*" (Pergamon, London, 1966).
9. E. Cartmell and G. W. A. Fowles, "*Valency and Molecular Structure*" (Butterworths, London, 1966).
10. L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory" (Methuen, London, 1960).
11. R. W. G. Wyckoff, "*Crystal Structures*" (Wiley, N. Y., 1963)
12. J. Brynestad and H. L. Yakel, *Inorg. Chem.*, **17**, 1376 (1978); H. L. Yakel and J. Brynestad, *Inorg. Chem.*, **17**, 3294 (1978).
13. S. Cummings, J. E. Enderby and R. A. Howe, *J. Phys. C.*, **13**, 1, (1980).
14. N. A. Hewish, G. W. Neilson and J. E. Enderby, *Nature*, **297**, 138 (1982).
15. N. A. Hewish, J. E. Enderby and W. S. Howells, *J. Phys. C* (to be published).
16. A. K. Dorosh and A. F. Skryshevskii, *J. Struct. Chem.* **8**, 300 (1967).
17. D. R. Sandstrom, *J. Chem. Phys.*, **71**, 2381 (1979).
18. J. R. Newsome, G. W. Neilson, J. E. Enderby and M. Sandstrom *Chem. Phys. Lett.*, **82**, 399 (1981).
19. G. W. Neilson, *J. Phys. C.*, **15**, L233 (1982).
20. A. Fontaine, P. Lagarde, D. Raoux, M. P. Fontana, G. Maisario, P. Migliardo and F. Wanderlingh, *Phys. Rev. Lett.*, **41**, 504 (1978).
21. P. Lagarde, A. Fontaine, D. Raoux, A. Sadoc and P. Migliardo, *J. Chem. Phys.*, **72**, 3061 (1980).
22. R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 463 (1941).
23. R. A. Robinson and R. H. Stokes, "*Electrolyte Solutions*". (Butterworth: London, 1955)
24. D. L. Wertz and J. R. Bell, *J. Inorg. Nucl. Chem.*, **35**, 137 (1973); **35**, 861 (1973). ibid.
25. R. F. Kruh and G. L. Standley, *Inorg. Chem.*, **1**, 941 (1962).
26. G. Palinkas and E. Kalman, *Z. Naturforsch.*, **36A**, 1367 (1981).
27. D. E. Irish, B. McCarroll and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).
28. D. F. C. Morris, E. L. Short and D. N. Waters, *J. Inorg. Nucl. Chem.*, **25**, 975 (1963).
29. M. P. Fontana, G. Maisano, P. Migliardo and F. Wanderlingh, *J. Chem. Phys.*, **69**, 676 (1978).
30. F. Aliotta, G. Galli, G. Maisano, P. Migliardo, C. Vasi and F. Wanderlingh, *Nuovo Cimento D* **2**, 103 (1983).
31. B. Gilbert, *Bull. Soc. Chim. Belges*, **76**, 493 (1967).
33. M. Sandström and G. Johansson, *Acta. Chem. Scand.*, **A31**, 132 (1977).
34. M. Sandström, *Acta Chem. Scand.*, **A31**, 141 (1977).
35. A. M. Hooper and D. W. James, *Aust. J. Chem.*, **24**, 1345 (1971).
36. J. W. Macklin and R. A. Plane, *Inorg. Chem.*, **9**, 821 (1970).