Concentrated Aqueous Solutions and Liquid Hydrates of Zinc Chloride: A Study of their Solvent Behaviour using Intershell, Charge-transfer, and *d–d* Absorption Spectra

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The u.v.–visible absorption spectra of Tl^+, Pb^{2+}, Co^{2+}, Ni^{2+}, VO^{2+}, and Fe^{3+} were examined in the $ZnCl_2$–H_2O system, with salt : water ratios ranging from 1 : 3 to 1 : 108. The spectral trends were compared with those in the $CaCl_2$–H_2O system, and they indicated that at low water contents, including compositions corresponding to the liquid salt hydrates, the two systems differ markedly. Whereas the $CaCl_2$–H_2O system furnishes a high concentration of Cl^- ions but very little water for co-ordination with solute metal ions, the $ZnCl_2$–H_2O system, in marked contrast, appears to contain water but virtually no 'free' chloride ions, any chloride co-ordinating to solute metal ions being in the form of part of a chlorozincate group.

Many salt hydrates melt to yield stable liquids whose properties are not necessarily those of dilute solutions extrapolated to higher concentration. For a halide, $MX_n{\cdot}6H_2O$ say, the liquid has a constitution which depends on equilibria such as (1)

$$[M(H_2O)_6]^{n+} + X^- \rightleftharpoons [M(H_2O)_5X]^{(n-1)+} + H_2O \quad (1)$$

When the hexa-aquo species predominates, the liquid contains an abundance of halide ions and little 'free' water, but when halogeno complexes predominate there is more water available but a lower concentration of 'free' halide ions. Thus, equilibria such as (1) will profoundly affect the properties of a molten salt hydrate, especially its behaviour towards electrophilic solutes such as metal ions or the conjugate acids of organic molecules (which might arise owing to the acidic nature of molten salt hydrates[1]).

The importance of molten salt hydrates is recognised[2–4] but little is known about their constitution and solvent properties. The present work examines the behaviour of the $ZnCl_2$–H_2O system towards Tl^+, Pb^{2+}, Co^{2+}, Ni^{2+}, VO^{2+}, and Fe^{3+} These ions were chosen because of their chemical importance and their reliability in signalling, spectroscopically, the host properties of a medium.[5,6] Zinc chloride forms the hydrates $ZnCl_2{\cdot}xH_2O$ where x = 1, 1.5, 2.5, 3, or 4, and these are liquids* at ambient temperature.[7] Solid $ZnCl_2$ consists of a network of zinc ions surrounded tetrahedrally by chloride ions, each serving to bridge two Zn^{2+} ions. This 'silica type' structure is only partially disrupted by water, and even in dilute solution fragments of the $>Zn(\mu\text{-}Cl)_2Zn<$ structure remain.[8] As a consequence, the liquid hydrate $ZnCl_2{\cdot}4H_2O$, for example, is expected to furnish few Cl^- ions but some 'free' water, contrasting with, for example, liquid $CaCl_2{\cdot}6H_2O$ (m.p. 29.9 °C) which appears to furnish much Cl^- but very little water (as shown by the conversion of $[Co(H_2O)_6]^{2+}$ into the tetrahedral chloro complex).[9] Metal ions in the $ZnCl_2$–H_2O system might form aquo complexes similar to the ones in aqueous solution, or they may form chloro complexes or complexes with a co-ordination sphere composed of both water and chloride. Also the $>Zn(\mu\text{-}Cl)_2Zn<$ units might co-ordinate through the chloride component, since this behaviour has been previously observed in anhydrous vitreous zinc chloride and shown to be distinct from the formation of normal chloro complexes.[10]

Experimental

The hydrates and concentrated aqueous solutions of zinc chloride were prepared and analysed by methods previously described,[1] while those of calcium chloride were prepared from AnalaR $CaCl_2{\cdot}6H_2O$ and analysed by estimating the chloride concentration with standard silver nitrate solution. Solutions of the metal ions were obtained by dissolution of the metal chloride, except in the case of VO^{2+} when the sulphate was used; sometimes dissolution was assisted by warming.

Absorption spectra were recorded using a Unicam SP700C spectrophotometer; 1-mm pathlength cells allowed ranges up to approximately 48 000 cm^{-1} to be obtained for the $ZnCl_2$–H_2O system and slightly beyond for the $CaCl_2$–H_2O system.

Results and Discussion

The s^2 *p*-block ions Tl^+, Pb^{2+}, and Bi^{3+} have u.v. absorption bands which are very sensitive to changes occurring in their co-ordination spheres. The lowest-energy Laporte-allowed transition for these ions, *s–p* $^1S_0 \longrightarrow {}^3P_1$, gives rise to a distinct absorption band which, despite being formally spin-forbidden, is very intense with an absorption coefficient of several thousand l mol^{-1} cm^{-1}. The $\nu_{max.}$ of this band is enormously red-shifted on going from the aquo ion ($\nu_{max.}$ 46 700 cm^{-1} for Tl^+ and 48 000 cm^{-1} for Pb^{2+}) to the chloro complex ($\nu_{max.}$ 40 500 cm^{-1} for Tl^+ and 36 800 cm^{-1} for Pb^{2+}). Mixed co-ordination spheres produce an 'average environment' effect,[10] so that the red shift is less, and this was observed for Tl^+ and Pb^{2+} in aqueous solutions of calcium chloride (salts of Bi^{3+} would not dissolve). For example, when $H_2O:CaCl_2$ = 108:1, $\nu_{max.}$ is 42 400 cm^{-1} for Tl^+, probably indicating that the predominant species is $[TlCl_4(H_2O)_2]^{3-}$, and for Pb^{2+} $\nu_{max.}$ is 38 200 cm^{-1}, suggesting $[PbCl_5(H_2O)]^{3-}$. As the $H_2O:CaCl_2$ ratio decreases, $\nu_{max.}$ decreases and approaches closely that of the all-chloro complex (see Figure 1). Also, the band becomes narrower, signifying that species other than the all-chloro species are present in very low concentration. Thus, in liquid $CaCl_2{\cdot}6H_2O$, Tl^+ and Pb^{2+} are present essentially as the chloro species, *e.g.* $[TlCl_6]^{5-}$ and $[PbCl_6]^{4-}$.

In dilute aqueous zinc chloride solutions (*e.g.* with $ZnCl_2$: H_2O = 1:108), the $\nu_{max.}$ values for Tl^+ and Pb^{2+} are greater

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* For such low-melting liquids, the term 'molten salt hydrates' is perhaps inappropriate and some workers have suggested that these and allied materials should be referred to as 'ionic liquids.'

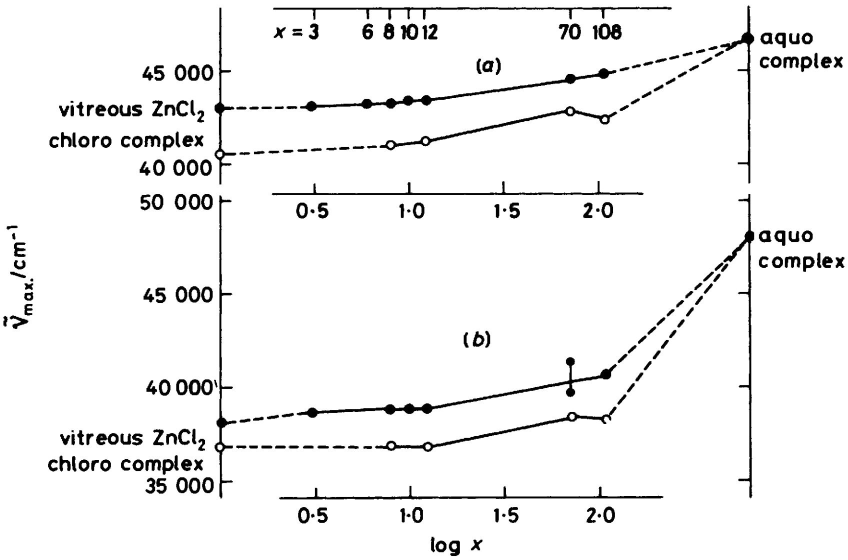

Figure 1. Plot of the frequency of the $^1S_0 \longrightarrow {}^3P_1$ absorption band of Tl^+ (*a*) and Pb^{2+} (*b*) *versus* log *x* in the $ZnCl_2$–H_2O (●) and $CaCl_2$–H_2O (○) systems (*x* = water:salt ratio)

Table. Absorption maxima (cm^{-1}) in the spectra of some transition-metal ions in aqueous and chloride media (oct. = octahedral, tet. = tetrahedral)

Metal ion	Transition	Aquo	Chloro	$ZnCl_2$[a]	$ZnCl_2\cdot4H_2O$	$CaCl_2\cdot6H_2O$
Co^{2+}(oct.)	$^4T_{1g} \longrightarrow {}^4T_{2g}$	8 000			8 000	
	$\longrightarrow {}^4A_{2g}$	16 000 (sh)			16 000 (sh)	
	$\longrightarrow {}^4T_{1g}$	19 700			19 500	
Co^{2+}(tet.)	$^4A_2 \longrightarrow {}^4T_1$		6 200	5 500 6 400		
	$\longrightarrow {}^4T_1(P)$		14 500 15 100 16 000	14 700 15 300 16 300		14 300 14 900 15 800
Ni^{2+}(oct.)	$^3A_{2g} \longrightarrow {}^3T_{2g}$	8 500		7 000	8 300	*ca.* 7 000
	$\longrightarrow {}^3T_{1g}$	13 800		10 500	13 500	12 200
	$\longrightarrow {}^1E_g$	15 200			14 800	
	$\longrightarrow {}^3T_{1g}(P)$	25 300		21 500	25 300	23 600
Ni^{2+}(tet.)	$^3T_1 \longrightarrow {}^3A_2$		7 400			
	$\longrightarrow {}^1E$		11 600			
	$\longrightarrow {}^3T_1(P)$		14 200 15 300			
$VO^{2+}(C_{4v})$	$^2B_2 \longrightarrow {}^2E(I)$	12 900			13 100	12 700
	$\longrightarrow {}^2B_1$	15 500 (sh)			*ca.* 15 000 (sh)	*ca.* 15 000 (sh)
Fe^{3+}(oct)	Charge transfer	42 000			>35 000[b]	
Fe^{3+}(tet.)	Charge transfer		27 300			27 300

[a] Vitreous $ZnCl_2$, data from ref. 6. [b] Unknown stereochemistry.

than in corresponding aqueous solutions of calcium chloride. The value of 44 900 cm^{-1} observed for Tl^+ suggests the species $[TlCl_2(H_2O)_4]^-$ and 40 600 cm^{-1} for Pb^{2+}, $[PbCl_4(H_2O)_2]^{2-}$. At much lower H_2O:$ZnCl_2$ ratios, the absorption band becomes narrower and $\nu_{max.}$ undergoes a red shift. However, $\nu_{max.}$ does not fall to the value expected for $[TlCl_6]^{5-}$ and $[PbCl_6]^{4-}$ as is the case for the $CaCl_2$–H_2O system. Instead it approaches a somewhat higher value (Figure 1) which has been observed previously in $ZnCl_2$ glass doped with these metal ions, where they are co-ordinated by chloride ions attached to the Zn^{2+} ions and for which $\nu_{max.}$ is 43 000 cm^{-1} for Tl^+ and 38 100 cm^{-1} for Pb^{2+}.[10] Thus, it is probable that Tl^+ and Pb^{2+} are similarly co-ordinated in the concentrated $ZnCl_2$ solutions. (We do not favour the alternative possibility that Tl^+ and Pb^{2+} are present as mixed chloroaquo complexes since it requires that the observed frequencies match those in vitreous $ZnCl_2$ for *both* cations.) When the chlorides are part of the network, they are polarised and the 'basicity moderating' effect[11,12] of the Zn^{2+} ions causes a lowering of their electron-donor power. As a result, the chloride ions impart a smaller orbital-expansion effect on the Tl^+ and Pb^{2+} ions and, as previously discussed,[5,10] this raises slightly the $\nu_{max.}$ of the $^1S_0 \longrightarrow {}^3P_1$ absorption band. In terms of the nephelauxetic parameter, *h*,[13] which is 2.0 for chloride ligands, the polarisation effect of the Zn^{2+} ions causes this value to fall somewhat and, since *h* is directly proportional to $\nu_{max.}$,[14] a red shift in the frequency results. (In oxide systems, the effect is much more pronounced and is used for measuring the 'optical basicity' of glasses, slags, *etc.*[5,15])

d–d Spectra are far less sensitive. For example, Co^{2+} in vitreous $ZnCl_2$ is tetrahedrally co-ordinated,[6,16] but *d–d* spectra do not distinguish the $[CoCl_4]^{2-}$ species from the corresponding species where the chlorides are polarised by Zn^{2+} ions. The

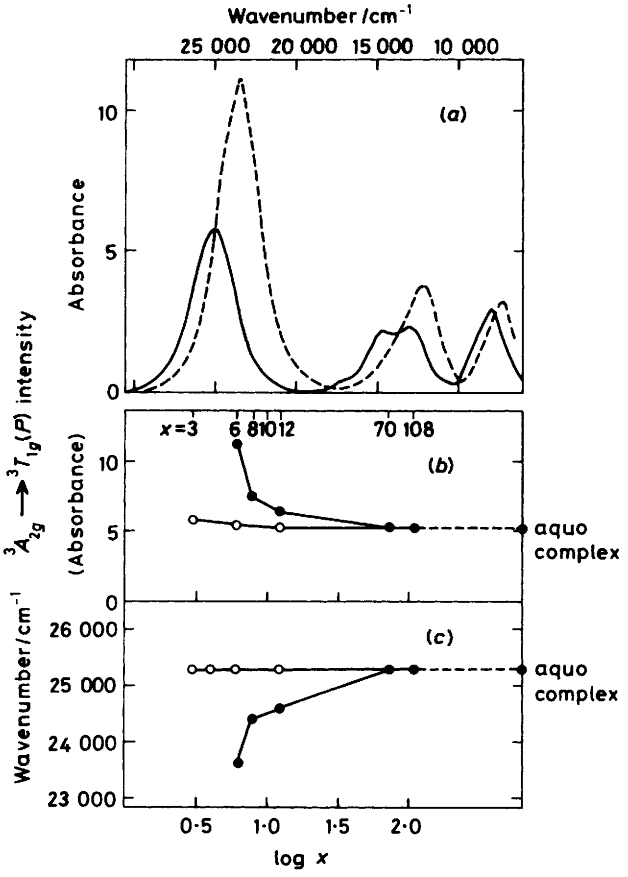

Figure 2. (*a*) Absorption spectra of Ni^{2+} in liquid $ZnCl_2{\cdot}4H_2O$ (full line) and $CaCl_2{\cdot}6H_2O$ (broken line); (*b*) changes in intensity of the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ band with log *x* in the $ZnCl_2$–H_2O (○) and $CaCl_2$–H_2O (●) systems (*x* = water:salt ratio); (*c*) changes in the frequency of the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ band

spectrum of Ni^{2+} in vitreous $ZnCl_2$ (Table) is significantly different from that of $[Ni(H_2O)_6]^{2+}$, especially the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ band which is lower by 3 800 cm^{-1}. It therefore follows that the spectrum of Ni^{2+} in $ZnCl_2{\cdot}4H_2O$ is not due to an octahedral chloro species, but is almost certainly due to the hexa-aquo complex which it closely resembles. In contrast, the spectrum of Ni^{2+} in $CaCl_2{\cdot}6H_2O$ is significantly different. Although typical of octahedral co-ordination, it is markedly red-shifted compared with the hexa-aquo ion [Figure 2(*a*)]. The most pronounced changes occur in the $^2A_{2g} \longrightarrow {}^3T_{1g}(P)$ band: in the $CaCl_2$–H_2O system, this band not only undergoes a red shift, but its intensity increases markedly [Figure 2(*b*) and (*c*)]. Both trends are consistent with the production of a mixed chloride–aquo co-ordination sphere of the predominating species. Previous studies[17] of the shift in the $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ band suggest that the species $[NiCl_2(H_2O)_4]$ is consistent with the observed $\nu_{max.}$ in $CaCl_2{\cdot}6H_2O$ (Table).

Like Ni^{2+}, Co^{2+} forms the aquo ion in the $ZnCl_2$–H_2O system but the chloro complex in the $CaCl_2$–H_2O system.[9] Presumably the higher charge/surface area ratio of Co^{2+} and Ni^{2+}, compared with Ca^{2+}, favours incorporation of chloride into their co-ordination spheres. The VO^{2+} ion has the dipositive charge spread over a greater surface area, and it appears to exist as $[VO(H_2O)_5]^{2+}$ (Table) in *both* solvent systems.

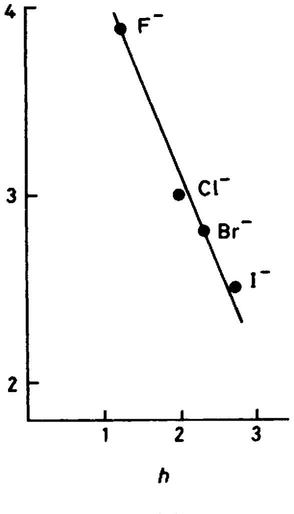

Figure 3. Plot of optical electronegativity, χ_{opt}, *versus* nephelauxetic parameter, *h*, for the halide ions. Values are from ref. 13, except for the revised *h* value for F^- which is from A. J. Bruce and J. A. Duffy, *J. Chem. Soc., Faraday Trans. 1*, 1982, 907

Charge-transfer Spectra.—The first Laporte-allowed absorption band arising from transference of an electron from ligand to central ion has a frequency (after adjusting for spin pairing and crystal-field energy, if necessary) given by equation (2)[13] where ν is in cm^{-1} and χ_{opt}(ligand) and χ_{opt}(central ion) are

$$\nu = 30\,000[\chi_{opt}(\text{ligand}) - \chi_{opt}(\text{central ion})] \quad (2)$$

the optical electronegativities. On the whole, the charge-transfer frequencies, ν, of complex ions conform well to this parametrisation. The magnitude of the optical electronegativities represents, in energy terms, (*i*) the ease with which the electron can be transferred to the central ion, and (*ii*) the difficulty of removing the electron from the ligand. If a ligand becomes polarised, it is expected that removing an electron would become more difficult. Since polarisation also results in a lowering of the orbital expansion parameter *h*, it might be expected that there is some quantitative relationship between χ_{opt}(ligand) and *h* for a ligand in various states of polarisation. This has been observed for oxide systems for which the relationship (3) holds fairly well.[18,19] For example, when an

$$\chi_{opt}(\text{oxide}) = 4.30 - 0.80h(\text{oxide}) \quad (3)$$

oxide is polarised by two protons, that is, when we are considering the aquo ligand, χ_{opt} is 3.5 and *h* is 1.0; on the other hand, in a borate glass, where polarisation is caused by boron(III), χ_{opt} is 3.15 and *h* is 1.46.[18] Equation (3) is very useful since it allows us to predict from orbital-expansion data (for example, shifts in the $^1S_0 \longrightarrow {}^3P_1$ frequency of s^2 *p*-block ions) the frequencies of charge-transfer bands of transition metal and other ions dissolved in oxide media.[19] The phenomenon has not been investigated for anions other than oxide, unfortunately, and so it is not possible to use the data of Pb^{2+} and Tl^+ in the $ZnCl_2$–H_2O system to estimate the frequencies of charge-transfer bands of metal ions complexed by Cl^- ions that are polarised by Zn^{2+} ions. As a guide to possible future work, it is worth noting that there is a roughly linear relationship between *h* and χ_{opt} for the four halide ions (Figure 3), such that equation (4) applies, which means that if polarisation causes a fall from

$$\chi_{opt}(\text{halide}) = 5.1—1.0h(\text{halide}) \quad (4)$$

2.0 to 1.8 for chloride, χ_{opt} increases by 0.2, which corresponds to an increase in 6 000 cm^{-1} in $\nu_{max.}$ of the first charge-transfer band ($\nu_{\max.}$ would be further blue-shifted in several transition-metal ions because of the larger Racah parameter B in the spin-pairing correction). This effect might be responsible for the pale yellow solution of Fe^{3+} in liquid $ZnCl_2{\cdot}4H_2O$ not displaying its first charge-transfer band below the absorption edge (observed at *ca.* 35 000 cm^{-1}, see Table), whereas in $CaCl_2{\cdot}6H_2O$, $\nu_{\max.}$ is at 27 300 cm^{-1} in accordance with the existence of $[FeCl_4]^-$.

Conclusions

The hydrates and highly concentrated aqueous solutions of zinc chloride differ from the $CaCl_2$–H_2O system by having available for the co-ordination spheres of dissolved metal ions (*i*) more 'free' water, (*ii*) virtually no 'free' chloride ions, and (*iii*) chloride ions which are part of the Cl–Zn network structure.

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