JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 193–196

Study of Ti (III) solutions in various molten alkali chlorides. II. Raman spectroscopy investigation

E. CHASSAING, F. BASILE, G. LORTHIOIR

Centre d'Etudes de Chimie Métallurgique (CNRS), 15 rue G. Urbain, 94400 Vitry/Seine, France

Received 13 May 1980

Raman spectroscopic investigation of Ti(III) solutions in various alkali metal chlorides and mixtures shows that the solvent cations affect the nature of the complex anions formed. We have studied in detail the effect of adding lithium chloride upon the anion $TiCl_6^{3-}$, which is the only species present in Ti(III) solutions in molten caesium chlorides at 700° C. At 20 mol% LiCl a new band appears in the $TiCl_6^{3-}$ spectrum, and it becomes the most important one from 80% LiCl onwards. This line cannot be associated with any vibration of $TiCl_6^{3-}$ nor $TiCl_4^-$ but could be attributed to the condensed form $Ti_2Cl_9^{3-}$.

---

1. Introduction

There have been few studies on the nature of Ti(III) species in molten baths except those of Gruen and MacBeth [1] who reported the electronic absorption spectra of some transition metals. These authors showed that in alkali metal chloride melts the trivalent ions of 3d metals such as Ti^{3+} could exist as the tetra- or hexa-coordinated forms in equilibrium:

$$TiCl_6^{3-} \rightleftharpoons TiCl_4^- + 2Cl^-.$$

However, in these same media Ti^{2+} could only exist in the tetrahedral form $TiCl_4^{2-}$, whereas in aluminium chloride it is hexa-coordinated [2].

We therefore undertook to determine the structure of the titanium complexes present in the alkali metal chloride mixtures studied in the first part of this work [3]. To this end Raman spectroscopy can be used for the identification of the species in baths from the solid state up to the melting point or even beyond. The experimental techniques are the same as those previously described [4].

2. Study of pure Ti(III) compounds

For comparison we have collected in Table 1 the Raman frequency vibrations of different pure titanium compounds. The only well-known tetracoordinated titanium compound is the tetrachloride $TiCl_4$, whose spectrum has been recorded both in the vapour and the liquid phase and has been indexed in terms of tetrahedral symmetry T_d [5]. In previous studies we have recorded the spectra of the hexa-coordinated compounds K_2TiCl_6, K_3TiCl_6 and Cs_3TiCl_6. The bands have been assigned by analogy with those of caesium hexachlorotitanate $Cs_2Ti^{IV}Cl_6$ studied by Van Bronswyk *et al.* [6]. In a regular octahedral site there are six fundamental modes; three are Raman active $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(t_{2g})$, whereas $\nu_3(t_{1u})$ and $\nu_4(t_{1u})$ are infrared active and $\nu_6(t_{2u})$ is inactive. Literature data indicate that in the case of Cs_2TiCl_6 the ν_3 and ν_4 vibrations are active in the infrared and also in the Raman [6, 7]. This shows therefore that the $TiCl_6^{2-}$ anion is of lower symmetry than a regular octahedron and that it no longer has a centre of symmetry. In the same way Cs_3TiCl_6 shows the two bands ν_3 and ν_4 in the Raman spectrum (Fig. 1); these are normally inactive. On the other hand the ν_2 line does not appear but it is often very weak or even absent in hexahalide complexes of groups IVb and Vb [6]. The ν_3 line does not exist in potassium compounds. The ν_4 appears in K_2TiCl_6 but not in K_3TiCl_6. It is worth pointing out that, for the same oxidation state, the ν_1 line shifts towards higher frequencies (+ 10 cm^{-1}) on going from Cs to K; for the same counterion its frequency decreases by 30 cm^{-1} on going from oxidation states IV to III.

We were unable to obtain the Raman spectra of

0021–891X/81/020193–04$02.40/0

Table 1. Raman frequencies of pure compounds. The figures in brackets are infrared frequencies

Compound	*Point group*	$\nu_3(t_2)$	$\nu_1(a_1)$	$\nu_4(t_2)$	$\nu_2(e)$		*Reference*
$TiCl_4$	T_d	498	489	136	114		[5]
		$\nu_3(t_{1u})$	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_4(t_{1u})$	$\nu_5(t_{2g})$	
Cs_2TiCl_6	O_h	334 (345)	320	272	190 (190)	186	[6] [7]
K_2TiCl_6	O_h	– (350)	330	–	180	150	[8]
Cs_3TiCl_6	O_h	330	290	–	180	150	
K_3TiCl_6	O_h	–	300	–	–	160	

the condensed form $M_3Ti_2Cl_9$ (M = K or Cs) in which the titanium is always hexa-coordinated but where one face of the octahedron is shared. This failure is no doubt related to the very deep green colour of these complexes. Probably for the same reason, Fraser *et al.* [9] could not obtain the spectrum of the violet α form of $TiCl_3$ which we use to feed our baths. Our own attempts were, moreover, equally unsuccessful.

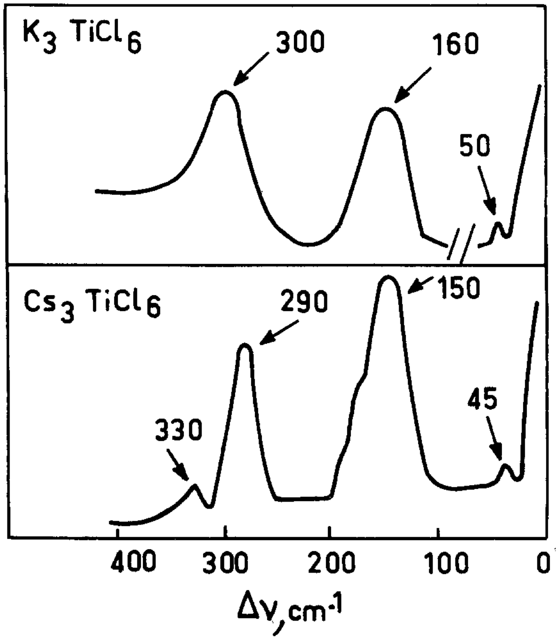

Fig. 1. Raman shifts for K_3TiCl_6 and Cs_3TiCl_6. Temperature = 25° C, λ = 514.5 nm.

3. Study of Ti(III) solutions in various alkali metal chlorides and mixtures

The molar fractions of the Ti(III) solutions were between 1×10^{-2} and 5×10^{-2}, i.e. within the range studied in the chemical experiments of Part 1 [3] (0.3×10^{-2} to 10×10^{-2}). These limits are imposed by spectroscopic features: with lower concentrations no Raman signal is obtained; with higher concentrations the resulting solutions are too dark and so the absorption of the incident light is too strong and no scattered light comes out.

The spectra of solutions of Ti(III) in three of the baths studied previously reveal that the relative intensities and the positions of the bands depend on the solvent (Fig. 2). In pure molten caesium chloride at 700° C (Fig. 2c) the spectrum is identical with that of Cs_3TiCl_6. In KCl–LiCl the spectrum is not so well defined; it has a shoulder at 160 cm^{-1} and a band at 280 cm^{-1}, that is, at a lower frequency than that of the ν_1 vibration of K_3TiCl_6 (300 cm^{-1}). The spectrum is even worse in molten lithium chloride because of strong fluorescence, but there is a shoulder at the same frequency (280 cm^{-1}) as in the previous eutectic.

In order to determine the reason for this variation we studied the spectra of Ti(III) solutions in binary mixtures of composition xCsCl/ $(1 - x)$ LiCl. Fig. 3 indicates a dependency on the solvent composition. As soon as a little lithium chloride is added to the caesium chloride a new band appears at 270 cm^{-1} and the ν_3 and ν_1 bands shift towards higher frequencies (Fig. 3b). When the lithium chloride content rises from 20 to 60 mol% the spectra remain similar though less well defined, the ν_1 line shifting towards 310 cm^{-1}

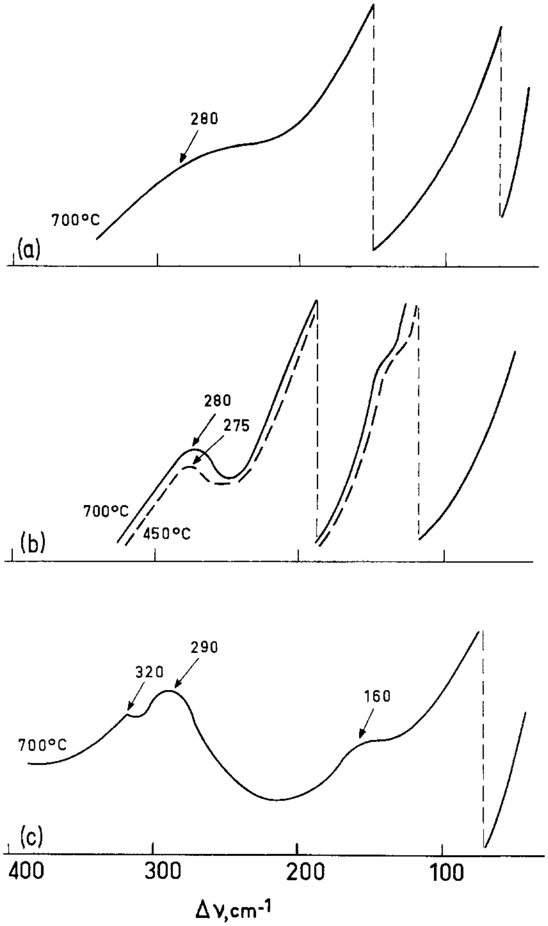

Fig. 2. Raman shifts for Ti(III) solutions in various chlorides. (a) LiCl, (b) KCl–LiCl (40.5–59.5 mol%), (c) CsCl.

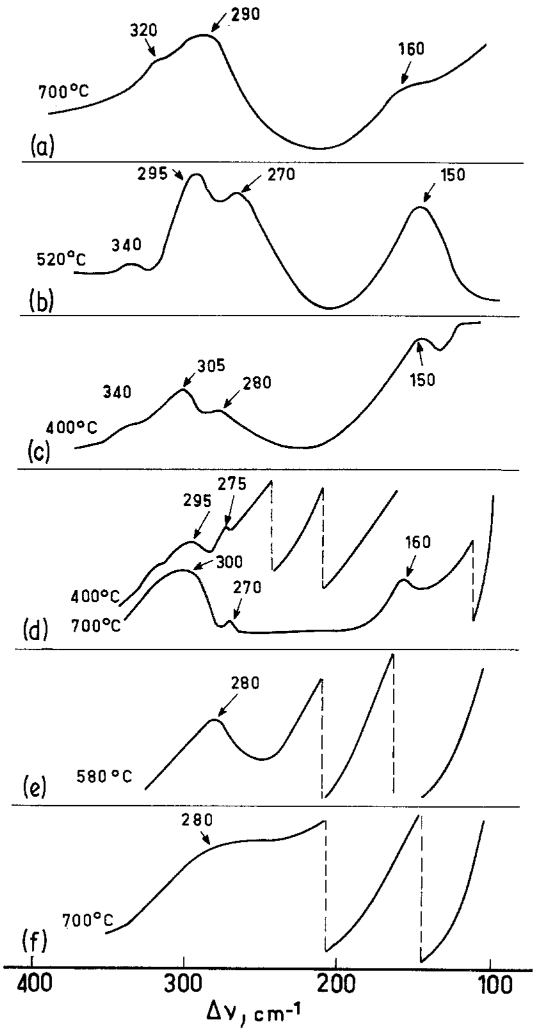

Fig. 3. Raman shifts for Ti(III) solutions in binary mixtures of LiCl and CsCl. (a) CsCl, (b) 80% CsCl–20% LiCl, (c) 60% CsCl–40% LiCl, (d) 40% CsCl–60% LiCl, (e) 20% CsCl–80% LiCl, (f) LiCl.

while ν_3 diminishes. Only the new band at 280 $\mathrm{cm^{-1}}$ persists above 80 mol% (Figs 3e and f). It is situated at the same frequency as that of the main signal observed in the KCl–LiCl eutectic with 60 mol% of lithium chloride (Fig. 2b).

These spectral changes are due to a modification of the symmetry of the Ti(III) complexes in these mixtures. It is unlikely that the band which appears at 270 $\mathrm{cm^{-1}}$ corresponds to the ν_2 vibration, present only in the spectrum of $\mathrm{Cs_2TiCl_6}$, since we did not observe it for the other titanium IV and III complexes (Table 1). Moreover, the strongest line of a spectrum is generally the totally symmetric vibration ν_1 which shifts towards higher frequencies when the radius of the counterion decreases. Furthermore, if this line arose from the splitting of the ν_1 vibration, two bands should always be seen; this is not the case (Figs. 3e and f). Consequently this band could be due to the ν_1 vibration of a different configuration of $\mathrm{TiCl_6^{3-}}$. Indeed, there are two other complex anions of Ti(III): $\mathrm{TiCl_4^-}$ and $\mathrm{Ti_2Cl_9^{3-}}$. These two forms, containing fewer $\mathrm{Cl^-}$ ions, can exist in equilibrium with $\mathrm{TiCl_6^{3-}}$ according to the reactions:

$$\mathrm{TiCl_6^{3-} \rightleftharpoons TiCl_4^- + 2Cl^-} \qquad (1)$$

$$\mathrm{TiCl_6^{3-} \rightleftharpoons \tfrac{1}{2}Ti_2Cl_9^{3-} + \tfrac{3}{2}Cl^-} \qquad (2)$$

When the lithium content of CsCl–LiCl mixtures is increased the acidity of the bath rises; that is, these media become more and more powerful as chloride ion acceptors. Equilibria 1 and 2 therefore tend to shift to the right. However, if the tetra-coordinated form $TiCl_4^-$ (Reaction 1) appeared, this would cause the ν_1 vibration to shift towards high wavenumbers [10]. This is what is observed for $TiCl_4$, whose ν_1 vibration is at 390 cm^{-1} (Table 1). Now, the extra line appears at a slightly lower frequency than that of the ν_1 vibration of $TiCl_6$ symmetry. Consequently, the configuration which arises when lithium chloride is added could be that of $Ti_2Cl_9^{3-}$, a condensed form in which two $TiCl_6$ octahedra are joined by one face. The fact that each titanium has an octahedral environment in the two configurations would explain the small difference in the position of the main band in the two species (275 and 290 cm^{-1}).

References

[1] D. M. Gruen and R. L. MacBeth, *Pure Appl. Chem.* 6 (1963) 23.
[2] H. A. Øye and D. M. Gruen, *Inorg. Chem.* 3 (1964) 836.
[3] E. Chassaing, F. Basile and G. Lorthioir, *J. Appl. Electrochem.* **11** (1981) 187.
[4] E. Chassaing, G. Lucazeau and G. Lorthioir, *Z. Anorg. Allg. Chemie* **468** (1980) 235.
[5] R. J. H. Clark, B. K. Hunter and D. M. Rippon, *Inorg. Chem.* 11 (1972) 56.
[6] W. van Bronswyk, R. J. H. Clark and L. Maresca, *Inorg. Chem.* 8 (1969) 1395.
[7] E. Wendling and R. Rohmer, *Bull. Soc. Chim. France* 1 (1967) 8.
[8] D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc.* (1967) 100.
[9] G. V. Fraser, J. M. Chalmers, V. Charlton and M. E. A. Cudby, *Solid State Commun.* 21 (1977) 933.
[10] B. Gilbert, G. Mamantov and G. M. Begun, *J. Chem. Phys.* 62 (1975) 950.