

Raman Spectral Study of WCl_6 in Al_2Cl_6 and Chloroaluminate Melts

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Received September 27, 1982

The chemical and electrochemical behavior of solute species in chloroaluminate melts [1] depends on acid–base properties of the solvent which for the $AlCl_3$–NaCl system are determined by the $AlCl_3$/NaCl ratio and temperature. We have been studying the electrochemistry of refractory metals in these media. It has been shown that the electrochemical reductions of Nb(V) [2], Ta(V) [3], and W(VI) [4] are very complex processes and result in the formation of clusters. Raman spectral studies of pentavalent niobium [5] and tantalum [6] have shown that these species exist as XCl_6^-, XCl_5 or X_2Cl_{10} (X = Nb, Ta) depending on the melt composition and temperature. Results of a similar study for hexavalent tungsten are presented below.

Experimental

$AlCl_3$ (anhydrous and iron-free from Fluka AG) was purified by sublimation after being kept molten in contact with high purity aluminum metal (m5N from Alfa) for 24 hours at 210 °C. NaCl (Fisher) was dried for 72 hours at 400 °C under vacuum. Further purification of the equimolar mixture of $AlCl_3$ and NaCl was carried out by constant current electrolysis [7]. Sublimed $AlCl_3$ was added to the equimolar melt to prepare acidic $AlCl_3$–NaCl melts, such as $AlCl_3$–NaCl (63–37 mol percent ≡ 63/37) and 52/48 melts. WCl_6 (from Alfa) was purified by sublimation at 210 °C. Raman cells were made from square Pyrex tubing (5 × 5 mm). Salts

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**Operated for the U.S. Department of Energy by the Union Carbide Corporation.

TABLE I. Raman Frequencies (cm^{-1}) for Various WCl_6 Containing Media with Assignments.

[a]WCl_6 85 *mF* Al_2Cl_6 215 °C 603.4 nm Ex.		[b]WCl_6 130 *mF* $AlCl_3$/NaCl (63/37) 238 °C 602.1 nm Ex.		WCl_6 134 *mF* $AlCl_3$/NaCl (52/48) 238 °C 602.1 nm Ex.		[c]WCl_6 128 *mF* $AlCl_3$/NaCl$_{sat.}$ 243 °C 602.1 nm Ex.		WCl_6 in $CHCl_3$ 23 °C 514.5 nm Ex.		WCl_6 solid Van Bronswyk *et al.* Ref. 11		WCl_6 gas Beattie and Ozin in Ref. 11		WCl_6 in liquid Cl_2 Creighton Ref. 9		WCl_6 in CH_3NO_2 Brown *et al.* Ref. 10	
102 s,p	A	96 m	B														
116 s,dp	A			118 m	C	118 m	C										
~150 w	ν_5	~150 m	ν_5	~150 mw	ν_5	~150 mw	ν_5			164 w	ν_5	163 w	ν_5	209 m	ν_5	182	ν_5
166 w,dp	A	163 m	B,C	182 m	C	180 m	C										
218 m,p	A																
283 w	A	311 s	B	312 w	B	~310 vw	ν_2			315 vw	ν_2	325 w	ν_2	317 m	ν_2	331 vw	ν_2
340 vs,p	A	348 s	C	348 s	C	349 vs	C										
406 m,p	ν_1	410 s	ν_1	409 m	ν_1	410 m	ν_1	407	ν_1	410 s	ν_1	400 s,p	ν_1	409 vs,p	ν_1	437	ν_1
510 w	A	437 m	B	~437 vw	B												
605 w	A	~490 w	C	~490 w	C	~490 w	C										

[a]Fig. 1a. [b]Fig. 1b. [c]Fig. 1c. Assignments; A, Al_2Cl_6; B, $Al_2Cl_7^-$; C. $AlCl_4^-$; ν_1, ν_2, ν_5 – WCl_6. s, strong; m, medium; w, weak; v, very; p, polarized; dp, highly depolarized; Ex.–excitation frequency.

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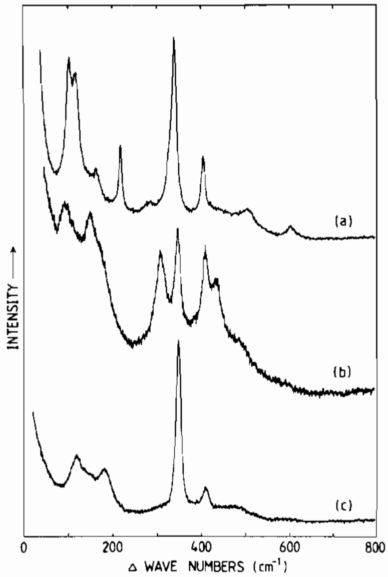

Fig. 1. Raman spectra (excitation ~ 602 nm) of WCl_6 dissolved in (a) Al_2Cl_6 melt. WCl_6 0.085 F., 215 °C. (b) $AlCl_3$–NaCl (63–37 mol %) melt. WCl_6 0.13 F., 238 °C. (c) NaCl–Saturated $AlCl_3$–NaCl melt. WCl_6 0.128 F., 243 °C.

were handled in a nitrogen filled dry box with water content below 2 ppm. Raman cells were sealed under vacuum after loading the sample.

A Ramanor HG-2S spectrophotometer (Instruments S.A.) equipped with concave, aberration corrected, halographic gratings was used to record the Raman spectra. This instrument employs a double monochromator, a photomultiplier tube for light detection, and photon counting electronics. Spectra were accumulated with a Nicolet Model 1170 signal averager which allowed repetitive scanning to increase the signal to noise ratio. Spectra were observed at an angle of 90° to the exciting laser light. The monochromator slits were parallel to the plane formed by the exciting and observed Raman light. Polarization measurements were made by rotating the plane of polarization of the exciting laser light by 90°. To excite the spectra an argon ion laser (Spectra-Physics Model 164) was used to pump a tunable dye laser (Coherent Radiation Model 590) containing rhodamine-6G dye.

Results and Discussion

Tungsten hexachloride has an octahedral (O_h) structure [8] with six normal modes of vibration. Of these vibrations, ν_1 (polarized), ν_2 and ν_5 are Raman active, ν_3 and ν_4 are infrared active and ν_6 is inactive. Raman spectra for WCl_6 dissolved in molten Al_2Cl_6, 63/37 $AlCl_3$–NaCl and the basic $AlCl_3$–$NaCl_{sat.}$ melt [1] are shown in Fig. 1. The observed band frequencies, relative intensities, and our assignments are listed in Table I. The Table also includes our results for WCl_6 dissolved in the 52/48 melt and chloroform, as well as data taken from the literature for WCl_6 in liquid Cl_2 [9], in liquid nitromethane [10] and for solid and gaseous WCl_6 [11]. It is apparent that the frequency of the strongest Raman band of WCl_6 (ν_1) is essentially the same (~410 cm^{-1}) regardless of the medium or physical state (solid or liquid). Little can be concluded from the other two Raman active bands, ν_2 and ν_5, because they are quite weak and overlap the solvent bands. The relative constancy of the ν_1 frequency of WCl_6 compared to spectral shifts with melt composition of 15–40 cm^{-1} for Ta(V) and Nb(V) species [5, 6], provides evidence that WCl_6 is present as a molecular entity and does not interact significantly with molten Al_2Cl_6 or chloroaluminate melts. Thus its behavior in chloroaluminate melts is similar to that of S_8 and I_2 [12, 13]. The intensity of the 409 cm^{-1} band of WCl_6 in chloroaluminate melts was found to increase with temperature and with melt acidity (Fig. 1). This behavior is also similar to that observed for S_8 and I_2 in molten chloroaluminates [12, 13].

In summary, the Raman results demonstrate that the predominant form of tungsten (VI) chloride in molten Al_2Cl_6 and $AlCl_3$–NaCl melts is WCl_6 and that the WCl_6 solubility increases with increase in the Lewis acidity of the solvent and with increasing temperatures.

Acknowledgement

This work was supported by the National Science Foundation Grant CHE77-21370, and the Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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