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ELECTRICAL CONDUCTIVITIES AND DEGREES OF IONIC DISSOCIATION OF 1:1 AND 1:2
ADDUCTS OF XENON DIFLUORIDE WITH ANTIMONY, TANTALUM AND NIOBIUM PENTA-
FLUORIDES IN THE MOLTEN STATE

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SUMMARY

Electrical conductivities of $[\text{XeF}_2 \cdot \text{MF}_5]$ and $[\text{XeF}_2 \cdot 2\text{MF}_5]$ ($M = \text{Sb, Ta, Nb}$) have been measured. These, together with viscosity measurements on $[\text{XeF}_2 \cdot \text{SbF}_5]$, which has the highest specific conductivity, leads to a value of the order of 11% for the degree of dissociation of the compounds near their melting points.

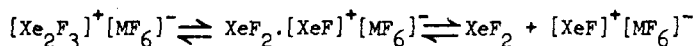
INTRODUCTION

It has been shown that, in the solid state, the adducts $[2\text{XeF}_2 \cdot \text{MF}_5]$, $[\text{XeF}_2 \cdot \text{MF}_5]$ and $[\text{XeF}_2 \cdot 2\text{MF}_5]$ ($M = \text{As, Sb, Nb, Ta, Pt, Ir}$ etc.)¹ can be thought of in terms of ionic formulations involving $[\text{Xe}_2\text{F}_3]^+$ and $[\text{XeF}]^+$ cations and the $[\text{MF}_6]^-$ and $[\text{M}_2\text{F}_{11}]^-$ anions. It is also clear that some of the compounds exhibit weak covalent interactions between the anion and the cation through fluorine bridges,²⁻⁴ and that the adducts should not, therefore, be regarded as salts. Indeed the crystal structure of $[\text{XeF}_2 \cdot 2\text{SbF}_5]$ ⁵ has shown that the xenon to bridging fluorine bond distance is 2.35\AA , which has been taken as

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evidence of considerable bond formation, and it has been suggested that the compound should be regarded as an essentially covalent molecule.⁵

Raman spectra of molten xenon difluoride - metal pentafluoride adducts⁶ have been interpreted to show that for the $[2XeF_2.MF_5]$ ($M = Sb, Ta$) adducts the following equilibrium occur:-



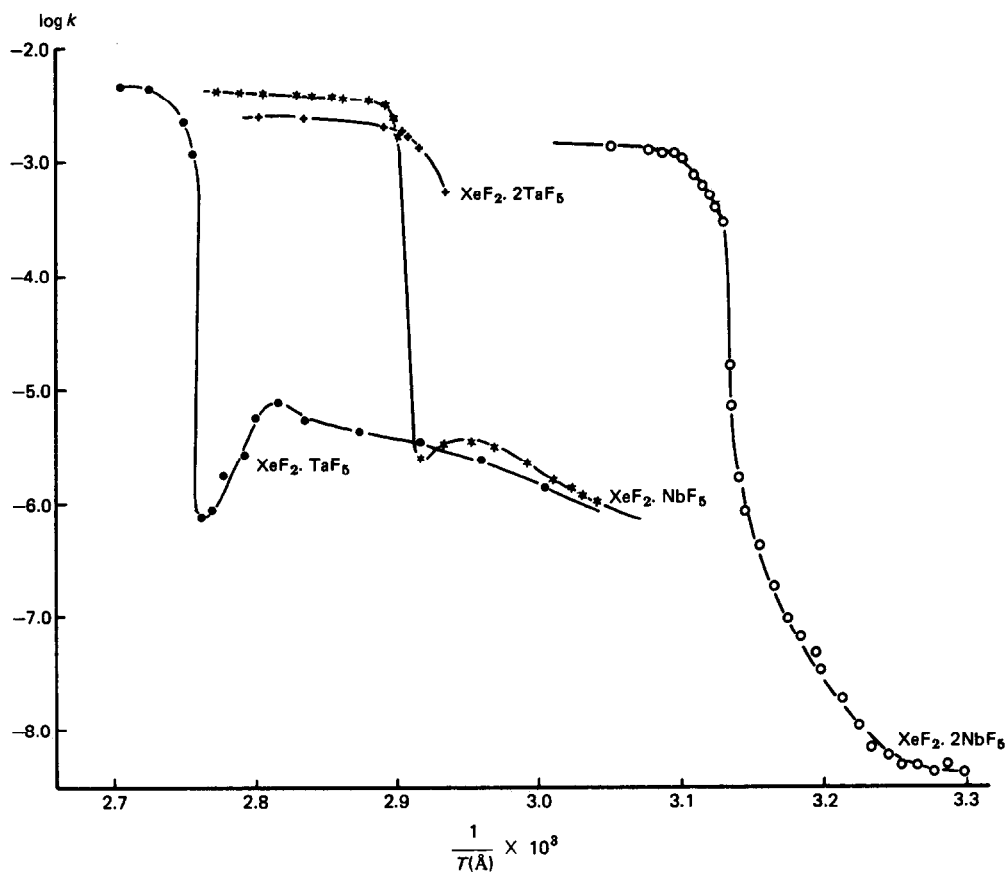
but in the $[XeF_2.MF_5]$ and $[XeF_2.2MF_5]$ ($M = Sb, Ta, Nb$) cases the molecular units in the melts are virtually the same as in the solids. A striking characteristic of the melt spectra for these latter two classes of adduct is the persistence of Raman peaks associated with the Xe...F and M...F bridging bonds. Indeed, the $\delta(F-Xe...F)$ bending modes are clearly visible in the spectra of most adducts.⁶

Although Greenwood and Martin have pointed out⁷ that the existence of a measurable conductivity in a molten compound does not necessarily mean that the conducting entities are ions or that such ions are characteristic of the melt. The Raman data on the melts of the $[XeF_2.MF_5]$ and $[XeF_2.2MF_5]$ ($M = Sb, Ta, Nb$) series suggest a considerable degree of ionic character (i.e. $[XeF]^+[MF_6]^-$ and $[XeF]^+[M_2F_{11}]^-$). It would be anticipated, therefore, that conduction in these compounds would occur entirely by virtue of their self-ionic dissociation and that the ions formed would be those evidenced in studies of the Raman spectra of the solids^{3,4} and the n.m.r. spectra of the solutions.⁸

In view of the intermediate character of the solid compounds with respect to their ionic-covalent character and in order to gain precise information on the constitution of the molten phase in these compounds, we have measured the specific conductivity of the two series. We have also determined the viscosity of the compound with the highest conductivity in order to estimate the percentage of ions free to conduct in the melt.

RESULTS AND DISCUSSION

Conductivity measurements on the purified compounds were made in pre-dried, prefluorinated cells with platinum electrodes. Measurements were made at regular intervals from up to 50° below the melting point and up to 30° beyond. Graphs of $\log k$ (specific conductivity) versus $1/T^\circ_K$ for the tantalum and niobium adducts are shown in Figure 1. The sharp decreases in conductivity, as the melting point is approached in several compounds, are presumably caused by phase changes in the solid state structures of the adducts.



TABLE

Specific conductivities for $[\text{XeF}_2 \cdot \text{MF}_5]$ and $[\text{XeF}_2 \cdot 2\text{MF}_5]$ (M = Sb, Ta, Nb) at their melting points.

Compound	Specific Conductivity $\times 10^4$ ($\text{ohm}^{-1} \text{cm}^{-1}$)	Melting Point, °
$[\text{XeF}_2 \cdot 2\text{SbF}_5]$	35.9	72-75
$[\text{XeF}_2 \cdot \text{SbF}_5]$	146.5	160-162
$[\text{XeF}_2 \cdot 2\text{TaF}_5]$	25.2	68-71.5
$[\text{XeF}_2 \cdot \text{TaF}_5]$	49.4	71-86
$[\text{XeF}_2 \cdot 2\text{NbF}_5]$	10.6	43-47
$[\text{XeF}_2 \cdot \text{NbF}_5]$	42.5	70-73

Specific conductivities at the melting point are summarized in the Table. The values are in the range $10\text{-}150 \times 10^{-4} \text{ ohm}^{-1} \text{cm}^{-1}$ and are, therefore, of the same order as alkyl ammonium picrates (at 150°),⁷ which are known to be incompletely dissociated, and also fall in the lower end of the range of values for boron trifluoride coordination compounds.⁷ The less conducting melts, and notably that of $\text{XeF}_2 \cdot 2\text{NbF}_5$, have specific conductivities only slightly higher than reported values for NbF_5 and TaF_5 .^{9,10}

It is significant that the specific conductivities for the two series of molten adducts is greatest for the antimony-containing compound and decreases successively when antimony is replaced first by tantalum and then by niobium. This is entirely in accord with the vibrational spectroscopic data on the solids⁴ and melts,⁶ which suggest that the greatest ionic character occurs in the antimony-containing compounds and fluorine bridging becomes increasingly significant in the tantalum and niobium adducts. This ionicity order for the solids has also been confirmed by thermochemical measurements.¹¹

Greenwood and Martin have shown⁷ that purified, molten boron trifluoride coordination compounds conduct entirely by virtue of their self-ionic dissociation and that, for uni-univalent electrolytes, the percentage degree of ionic dissociation (α) is approximately equal to the product of the molar conductivity ($\mu = \text{Mkd}^{-1}$) and the viscosity (η) (where M = molecular weight, k = specific conductivity and d = density). The viscosity can be derived from the product of the viscometer constant ($C_{(\text{visc})}$), the density (d) and the time of efflux (t) of the compound at the experimental temperature. The approximate percentage degree of ionic dissociation, therefore, can be obtained from the following expression:-

$$\alpha \approx \frac{Mk}{d} \cdot C_{(\text{visc})} d \cdot t = MkC_{(\text{visc})} t$$

This eliminates the necessity to have a measured density of the compound under investigation. (The densities of crystalline $[\text{XeF}_2 \cdot 2\text{SbF}_5]$ (3.69)⁵, XeF_2 (4.32)¹² and SbF_5 (4.07)¹³ suggest that a reasonable estimate for $[\text{XeF}_2 \cdot \text{SbF}_5]$ might be 3.8). Substitution of values ($M = 386$, $k = 0.01465 \text{ ohm}^{-1} \text{ cm}^{-1}$, $C = 0.32$, $t = 6.25 \text{ sec}$) gives a value of 11.31 for α at 162° . This value can only be regarded as approximate, but it establishes an order of magnitude for α for xenon difluoride adducts and might be regarded as an upper limit for the series of compounds under examination. The value is identical to the average degree of dissociation for tertiary alkyl ammonium picrates⁷ and shows that $[\text{XeF}_2 \cdot \text{SbF}_5]$ should be regarded as a weak electrolyte. The best-conducting picrates are the quaternary ammonium derivatives and it has been concluded that these, which have an average value of 48% for α , can be regarded as practically completely dissociated into ions.⁷

The results permit a further qualitative indication that other related adducts such as $[\text{SeF}_3 \cdot \text{SO}_3\text{F}]$ ($k_{\text{melt}} = 6 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$)¹⁴ and $[\text{SeF}_4 \cdot \text{MF}_5]$ ($M = \text{Sb, Ta, Nb and As}$)¹⁵ are also compounds with little ionic character in the melt or in solution.

EXPERIMENTAL

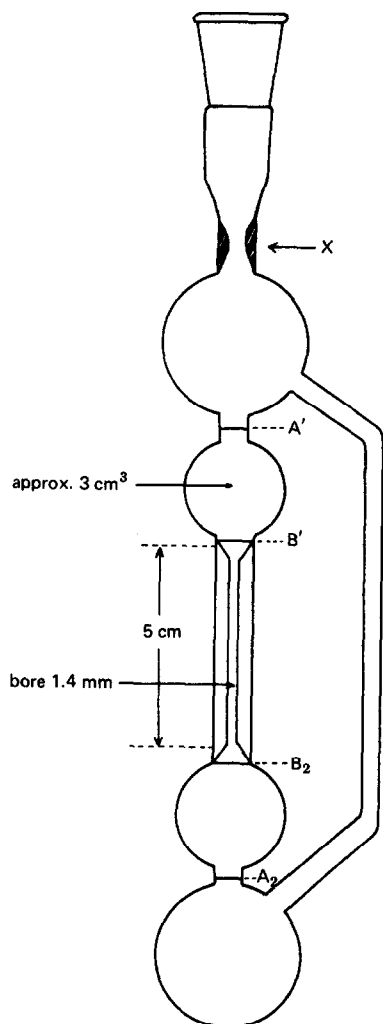
Adducts were prepared by melting stoichiometric quantities of the component molecules together under an atmosphere of dry xenon or nitrogen as outlined previously.⁴ The products were monitored for purity by Raman spectroscopy using a Coderg T800 spectrometer. Samples of the adducts were transferred to modified Mullard (type E.7597/A) conductivity cells which had been previously pumped to high vacuum and seasoned with fluorine. Preliminary experiments were carried out using a Wayne Kerr (type B221A) conductivity bridge but this was replaced by a Mark (type K1) digital bridge for subsequent measurements because it is better suited to the measurement of rapidly changing conductivities. The cell containing the sample was heated by a liquid paraffin bath at a rate between $1^{\circ} \text{ min}^{-1}$ and $0.2^{\circ} \text{ min}^{-1}$. Readings of conductivity, time and temperature were tabulated at 1° intervals except near the melting point when 0.5° intervals were used.

The conductivity cells were calibrated with a $N/50$ solution of analar KCl made up in deionised water.

The viscosity of $[\text{XeF}_2 \cdot \text{SbF}_5]$ was measured in a sealed, evacuated, Pyrex viscometer (Fig. 2) adapted from the early Ubbelohde design.¹⁶ Measurements were made with the viscometer totally immersed in an oil bath thermostated to $\pm 0.5^{\circ}$. The temperature was measured to within $\pm 0.1^{\circ}$ and the time of efflux to ± 0.1 sec. The viscometer was calibrated using both cyclohexanol and sulphuric acid (98% w/w). From tables of efflux time (t_o), density (d_o) and the known viscosity at the experimental temperature, the viscometer constant was calculated:

$$\text{Viscometer constant} = C_{(\text{visc})} = \eta_o (d_o t_o)^{-1}$$

The viscosity of the adduct was calculated using the viscometer constant, the observed efflux time and the estimated density at the melting point. Ten consistent values of the efflux time were obtained.



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