

**PROPERTIES OF THIONYL CHLORIDE SOLUTIONS (EXTENDED ABSTRACT)**

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Solutions of alkali metal tetrachloroaluminates in thionyl chloride (TC) exhibit very interesting physicochemical properties [1 - 3]. They have been studied mainly in connection with the development of the Ca-TC battery. It was recently found [4, 5] that replacing the  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte in the Ca-TC battery by either  $\text{Ba}(\text{AlCl}_4)_2$  or  $\text{Sr}(\text{AlCl}_4)_2$  resulted in a battery with a much longer shelf life. This is due to slower calcium corrosion. In these two electrolytes the chemical composition and properties of the SEIs which cover the calcium anode are different from that of the SEI in calcium tetrachloroaluminate. These modified SEIs provide better corrosion protection for the calcium anode than does the  $\text{CaCl}_2$  SEI in the  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte.

The purpose of this paper is to describe the physicochemical properties of TC solutions of calcium, strontium, and barium tetrachloroaluminates, with emphasis on the effect of  $\text{SO}_2$  on the solution properties.

At high salt concentrations in solvents of low dielectric constant, *e.g.*, TC ( $\epsilon \sim 9$ ), the predominant species are ionic aggregates [6]. In concentrated  $\text{MX}_2$ -type solutions in TC ( $\text{X} = \text{AlCl}_4^-$ ,  $\text{M}^{2+} = \text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) the smallest and most likely predominant charged ionic aggregates are  $\text{MX}^+$  and  $\text{MX}_3^-$  formed in the following reaction:



Accordingly, the equivalent conductivity is twice the molar conductivity. These ionic aggregates may be separated by molecules of the solvent (Y), ( $\text{MYX}^+$  and  $\text{XYMYX}^0$ , etc.) in equilibrium with ionic aggregates with no solvent molecules between the ions.

Density, viscosity and conductivity measurements were made at different  $\text{SO}_2$  concentrations in the range 0 - 50 vol.% over a temperature range of 10 - 70 °C and, in some cases, -30 - 230 °C. Over the range -30 to +70 °C for  $\text{MX}_2$ -TC solutions containing little or no  $\text{SO}_2$  and low salt concentrations, the conductivity increases in the order  $\text{Ca} > \text{Ba} > \text{Sr}$ . At low temperatures and high  $\text{SO}_2$  and  $\text{MX}_2$  concentrations the conductivity increases in the

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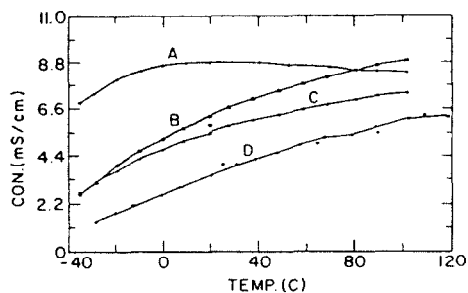


Fig. 1. Conductivities of 0.84 M  $\text{Ba}(\text{AlCl}_4)_2$  vs. temperature. A, 40%  $\text{SO}_2$ ; B, 20%  $\text{SO}_2$ ; C, 10%  $\text{SO}_2$ ; D, 0%  $\text{SO}_2$ .

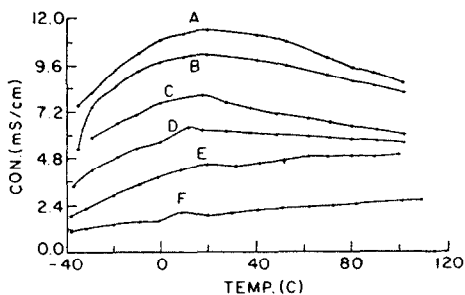


Fig. 2. Conductivities of 0.84 M  $\text{Sr}(\text{AlCl}_4)_2$  vs. temperature. A, 50%  $\text{SO}_2$ ; B, 40%  $\text{SO}_2$ ; C, 30%  $\text{SO}_2$ ; D, 20%  $\text{SO}_2$ ; E, 10%  $\text{SO}_2$ ; F, 0%  $\text{SO}_2$ .

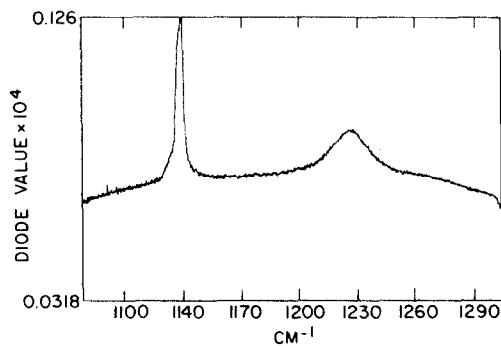


Fig. 3. Raman spectrum of  $\text{SOCl}_2$  containing 30%  $\text{SO}_2$ . The peak at  $1140 \text{ cm}^{-1}$  is assigned to  $\text{SO}_2$ .

order  $\text{Ca} > \text{Sr} > \text{Ba}$ . In  $\text{CaX}_2$  [2] and  $\text{SrX}_2$  solutions the conductivity increases monotonously with  $\text{SO}_2$  concentrations (Fig. 1). In most cases, the conductivity-temperature plot has a peak near room temperature [2] (Figs. 1 and 2) whose location depends on  $\text{SO}_2$  and  $\text{MX}_2$  concentrations. This means that at higher temperatures the conductivity decreases with temperature. In  $\text{BaX}_2$  solutions the effect of  $\text{SO}_2$  is more complex (Fig. 2). Increasing the concentration of  $\text{SO}_2$  to 50 vol.% results in an increase in conductivity of up to a factor of 8. The density and viscosity of these solutions increase in the order  $\text{Ba} < \text{Sr} \sim \text{Ca}$ . It is of interest to note that increasing the concentration of  $\text{SO}_2$  to 10 vol.% increases the density of 0.8 - 1.3 M  $\text{MX}_2$  solutions but does not significantly alter their viscosity. However, raising the concentration of  $\text{SO}_2$  to more than 20 vol.% results in a decrease of both viscosity and density. The equivalent conductivity (eqn. (1)) corrected for the change in the viscosity of  $\text{MX}_2\text{-TC-SO}_2$  solutions can be as high as  $100 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ .

Raman spectra measurements, taken at room temperature (Figs. 3 and 4) indicated the formation of a complex between  $\text{SO}_2$  and  $\text{M}^{2+}$ . The  $\text{M}(\text{SO}_2)_n^{2+}$  peak height increases with  $\text{SO}_2$  concentration. It seems that for

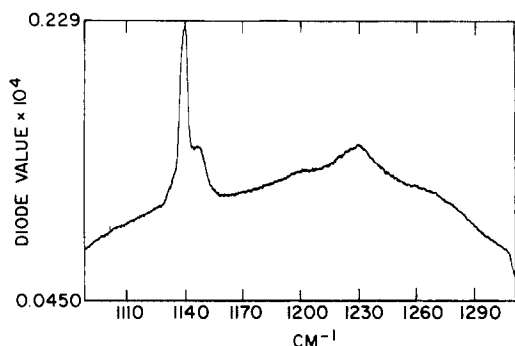


Fig. 4. Raman spectrum of 0.84 M  $\text{Sr}(\text{AlCl}_4)_2$  in  $\text{SOCl}_2$  containing 30%  $\text{SO}_2$ . The peak at  $1147 \text{ cm}^{-1}$  is assigned to the complex  $\text{M}(\text{SO}_2)_n^{2+}$ .

$\text{SrX}_2$  the maximum value of  $n$  is three. A smaller  $n$  value is estimated for  $\text{BaX}_2$  solutions. Our results can be interpreted as follows. The ionic migration in  $\text{MX}_2\text{-TC-SO}_2$  solutions takes place by two parallel mechanisms, a Stokesian and a non-Stokesian relay-type mechanism. The apparent negative energy of activation for conduction at high temperatures results from the breaking of ionic aggregates and shifting from solvent-separated ionic aggregates to intimate ionic aggregates. This should reduce the dissociation constants of the uncharged ionic aggregates (eqn. (1)) and, in addition, it should shorten the hopping range. The enhancement of conductivity by  $\text{SO}_2$  at low concentration is predominantly due to the formation of a larger  $\text{SO}_2\text{-M}^{2+}$  complex ion (or aggregate of such ions), and at high concentration is due to the decrease in the viscosity of the electrolytes.

## References

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