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AEC-NASA TECH BRIEF

Hydrated Multivalent Cations Are New Class of Molten Salt Mixtures

The problem:

To establish that aqueous mixtures of polyvalent ions, whose water content is insufficient to satisfy more than a first coordination sheath for the cations, are molten salt mixtures of weak-field cations. (Such mixtures consist of hydrated molten salts having independent, hydrated cations. These hydrated molten salts dissolve unhydrated salts in the same way that unhydrated molten salts usually dissolve each other.)

If the mixed nitrate–hydrate melt $Ca(NO_3)_2{\cdot}4H_2O + KNO_3$ is an aqueous molten salt mixture of weak-field cations, it should behave as follows: (1) its electrical conductivity should be completely analogous to that of other molten salt mixtures, (2) its theoretical glass transition temperature should vary in a manner opposite to that of the anhydrous system $Ca(NO_3)_2 + KNO_3$ and should increase with KNO_3 content (since the theoretical glass transition temperature for molten KNO_3 is greater than the experimental value for $Ca(NO_3)_2{\cdot}4H_2O$, and (3) its activation energy (Arrhenius coefficient) at a given temperature should increase with KNO_3 content.

The solution:

Electrical transport is exponentially dependent on $1/(T-T_0)$ in accord with the general equation for electrical conductance

$$\Lambda = AT^{1/2} \exp\left(-\frac{k}{T-T_0}\right)$$

where Λ is equivalent conductance, T_0 is the theoretical glass transition temperature, and k and A are constants. Since the value of k for the hydrated molten salt $Ca(NO_3)_2{\cdot}4H_2O$ is virtually the same as for the anhydrous molten salt mixture $Ca(NO_3)_2+KNO_3$, the same value of k is assumed for the mixed nitrate–hydrate melt $Ca(NO_3)_2{\cdot}4H_2O+KNO_3$.

A.R. grade $Ca(NO_3)_2{\cdot}4H_2O$ is fused without loss of water. Then the composition is changed by adding A.R. grade KNO_3, and the specific conductance is measured after each addition.

The activation energies increase rapidly with falling temperature. This increase occurs because the probability of ionic movement approaches zero at the theoretical glass transition temperature, rather than at 0°K as required by Arrhenius. The general equation for electrical conductance reduces to almost a single straight-line plot of activation energies for the systems $Ca(NO_3)_2{\cdot}4H_2O+KNO_3$ and $Ca(NO_3)_2+KNO_3$.

The theoretical glass transition temperature T_0 of the mixed nitrate–hydrate melt $Ca(NO_3)_2{\cdot}4H_2O+KNO_3$ increases with KNO_3 content, but the theoretical glass transition temperature of the anhydrous system $Ca(NO_3)_2+KNO_3$ decreases with KNO_3 content.

The activation energy of the mixed nitrate–hydrate melt increases with KNO_3 content.

Since the change in electrical conductance with concentration of KNO_3 is the same for both the mixed nitrate–hydrate melt $[Ca(NO_3)_2{\cdot}4H_2O+KNO_3]$ and the anhydrous mixture $[Ca(NO_3)_2+KNO_3]$, the mixed nitrate–hydrate melt closely resembles a molten salt mixture.

Notes:

1. The mixed nitrate–hydrate melt $Ca(NO_3)_2{\cdot}4H_2O+KNO_3$ is a representative hydrated mixture. It was selected because its anhydrous salt analogue, $Ca(NO_3)_2+KNO_3$, has been studied in some detail and because the electrical conductance of molten $Ca(NO_3)_2{\cdot}4H_2O$ has been measured recently.

(continued overleaf)

2. The temperature of the melt is measured by a precision mercury thermometer and checked by a fine-gage Cr/Al thermocouple attached to the conductance cell.
3. The resistance of the melt is measured at 3 kc and 1 kc with a silica dip-type cell with platinized electrodes, in conjunction with a precision conductance bridge. Calculations are based on the 3-kc readings, because the polarization errors are not sufficient to detectably affect results when resistance is greater than 1000 ohms.
4. Because of the low liquidus temperatures of the melt, this new class of molten salt mixtures may be useful for physicochemical investigations of molten salt behavior in a temperature range otherwise not readily accessible.
5. The general coherence of the experimental observations indicates that binary systems with hydrate components such as those of the system studied may be useful for investigating free volume-determined properties of ionic liquids.
6. Additional details are contained in: *Journal of the Electrochemical Society*, December 1965, vol. 112, no. 12, p. 1224–1227.
7. Inquiries concerning this innovation may be directed to:

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Patent status:

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