The Electric Conductivity of Molten (Na — Tl)NO₃ Mixtures

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Electrical conductivities and densities of molten (Na—Tl)NO₃ mixtures have been measured in the temperature range between 192 °C and 400 °C.

At all compositions the specific conductivities appear to be linear functions of the temperature. While the equivalent conductivities of the mixtures deviate negatively from additivity, the apparent activation energies \( \Delta E \) (from the relation \( \Lambda = \Lambda_0 \exp(-\Delta E/RT) \)) exhibit positive deviations from additivity.

This behavior is similar to that of other univalent binary systems with a common anion and seems to indicate that the polarization of the nitrate ion due to different cation sizes is the main cause of the additional hindrance to the electrical transport in mixtures.

In connection with other studies on the transport parameters of the (Na—Tl)NO₃ system¹, the electrical conductivity and the density of the system have been determined. In the literature the conductivity data of pure TlNO₃ present some discrepancies and few data on NaNO₃—TlNO₃ mixtures are available.²

Experimental

An U type cell with a great cell constant, without connection to the liquid of the thermostatic bath³ (thermoregulated to ±0.1 °C), was used. The bath, a (Li, Na, K) NO₃ eutectic mechanically stirred, was placed into a vertical Heraeus furnace. The temperature close to the cell was measured by means of a Cr—Al thermocouple, calibrated by comparison with a ITI* thermocouple of certified precision of ±0.1 °C.

The cell constant was determined by two different methods. First, H₂SO₄ solutions, titrated with 20/100 precision, whose conductivity values, precise to 1‰, were taken from the literature⁴, were employed. Second, the calibration was repeated employing molten KNO₃ utilizing conductivity data of Kroger and Weisssberger⁵. The cell constants were found to be 967.2 cm⁻¹ and 967.9 cm⁻¹, respectively.

Resistance measurements were carried out with a LKB precision bridge at 2000 c/sec. The additional polarisation resistances were considered negligible at this frequency⁶—⁸, taking into account the high cell constant. Accordingly very good agreement was found with the NaN₃ conductivities obtained by extrapolation to infinite frequency⁹.

Density measurements were carried out by the bob method, using a Mettler recording balance for the determination of the buoyancy of the bob. The temperature was measured by means of a certified Cr—Al thermocouple immersed in the melt close to the bob. Reagent grade salts, after three crystallisations from water, were used.

Results and Discussion

Conductivity measurements at six different concentrations (0.0; 0.141; 0.25; 0.50; 0.75; 1.0 mole fraction of TlNO₃) were carried out at temperatures ranging from 190 to 400 °C¹¹. Some runs were repeated several times in order to check the reproducibility. The experimental results are reported in Table 1. At each composition the specific conductivity was found to be a linear function of the temperature. The equations of the straight-lines, conductivity vs. \( T \), as determined by the least squares method, are reported in Table 2. The densities expressed in terms of straight-lines are given in Table 3.

¹ Work in preparation. Preliminary results have been presented at the 16th CITCE Meeting, Budapest, Sept. 5—10, 1965.
⁴ Istituto Termometrico Italiano, Torino (Italia).

For the liquidus curves of (Na—Tl)NO₃ see P. Franzosini and C. Sinistri, Ric. Sci. 3, 439 [1963].
Table 1. Experimental values of specific conductivity of NaN0₃ and TINO₃ and their binary mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of TINO₃</th>
<th>Temp. °C</th>
<th>$\chi$</th>
<th>Conductivity equations</th>
<th>Root mean square deviations °C</th>
<th>Temp. range °C</th>
</tr>
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<tbody>
<tr>
<td>0,00</td>
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<td>0,141</td>
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<td>1,00</td>
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</table>

Table 2. Equations for the specific conductivity of NaN0₃, TINO₃ and their binary mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of TINO₃</th>
<th>Density equations</th>
<th>Root mean square deviations</th>
<th>Temp. range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,00*</td>
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<td>0,141</td>
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<td>1,00</td>
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Table 3. Equations for the density of NaN0₃, TINO₃ and their binary mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of TINO₃</th>
<th>Density equations</th>
<th>Root mean square deviations</th>
<th>Temp. range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,00*</td>
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<tr>
<td>0,141</td>
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<td>0,75</td>
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<tr>
<td>1,00</td>
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</table>
The standard deviations $S$ were calculated by the formula 12:

$$S = \sqrt{\frac{\sum (\delta_n)^2}{(h-1)}},$$

where $\delta_n$ is the deviation of each measurement and $h$ the numbers of measurements.

The conductivities of pure NaN$_3$ and TINO$_3$ are plotted in Fig. 1, together with some recent literature conductivity data $^9, ^{13}$. The present NaN$_3$ values agree with those of other authors, while our TINO$_3$ values agree with those of De Nooijer $^9$ but differ by up to 4% from those collected by Janz $^{13}$.

Recently some specific conductivity data for TINO$_3$ and NaN$_3$ mixtures at three temperatures (200, 240, 320 °C) have been reported $^2$. While these data generally agree with ours at the two lower temperatures, they differ by about 3% in the range 0.25 $< X_{\text{Tl}} <$ 0.50 at 320 °C.

The specific conductivity isotherms corresponding to the equations of Table 2 are shown on the left hand side of Fig. 2. In the same figure the isotherms of the equivalent conductivity $A = \kappa V$ are presented.

The molar volumes, $V$, at each investigated composition were interpolated from the molar volumes calculated from the density equations of Table 3 (see Fig. 3).

According to the reported density data the molar volume isotherms do not deviate from additivity by

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more than + (0.15 cc ± 0.1)/mole. Our density data do not confirm those of PROTSENKO et al., who reported an S-shaped molar volume isotherm departing from a straight-line by about ± 1 cc/mole in the composition region of diluted mixtures.

The equivalent conductivity isotherms show rather marked negative deviations from additivity as compared with other binary nitrate systems containing NaN03.

From the relationship

\[ \log \lambda = \log \lambda_0 - \Delta E / R T, \quad (2) \]

the apparent activation energy \( \Delta E \) can be evaluated.

The \( \Delta E \) values calculated by the least squares method are reported in Table 4, with the standard deviations \( S_{\Delta E} \) calculated with the formula

\[ S_{\Delta E} = 1.986 \cdot S_{\log \lambda} \sqrt{h \sum 1/T_i^2} \sum 1/T_i^2, \quad (3) \]

where \( S_{\log \lambda} \) is the standard deviation of the function (2) calculated by a formula like the formula (1).

<table>
<thead>
<tr>
<th>Mole fraction of TINO3</th>
<th>0.00</th>
<th>0.14</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E ) (Kcal)</td>
<td>3.41</td>
<td>3.51</td>
<td>3.49</td>
<td>3.46</td>
<td>3.52</td>
<td>3.20</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.01</td>
<td>0.06</td>
<td>0.08</td>
<td>0.11</td>
<td>0.04</td>
<td>0.02</td>
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</tbody>
</table>

Table 4. Apparent activation energy of the system NaN03—TINO3.

The \( \Delta E \) values at all compositions lie in the range 3.55 ± 3.20 Kcal/mole, in rather good agreement with the activation energies of other nitrate systems.

In particular the value 3.40 Kcal/mole of NaN03 agrees with the value 3.215 reported by JANZ at temperatures up to 427°C, and with the values 3.35 ± 3.25 (at temperatures up to 450°C) of BIZOUARD. The 3.20 Kcal/mole value of TINO3 agrees with the value 3.16 that can be evaluated from the De NOOJER data and with the value 3.26 reported by JANZ.

The \( \Delta E \) values of mixtures are higher than those calculated additively from the activation energies of the pure components. This characteristic is a rather general one for systems the cations of which have different sizes, as can be seen in Fig. 4, which presents the excess activation energies of two series of

binary systems including NaN03 and TINO3 respectively; the conductivity data are taken from ref. 9.15.

The \( \Delta E \) deviations of the (Na—Tl)NO3 system are intermediate between those of the (Na—Cs)NO3 system and those (negligible) of the (Na—Ag)NO3 system. The (Na—Tl)NO3 system presents great deviations compared, for example, to the nearly ideal behaviour of the (Tl—Rb)NO3 system. From these trends one can conclude that this effect is the larger, the larger the difference between the cationic radii.

On the other hand KETELAAR, by investigating negative deviations of equivalent conductivity from additivity, has found that for a large number of equimolecular binary mixtures of monovalent nitrates these deviations are proportional to \( (\lambda_1 - \lambda_2)^2 / \lambda_1^2 \lambda_2^2 \), where \( \lambda = r_{cat} + r_{an} \). The polarisation energy term \( (1/\lambda_1^2 - 1/\lambda_2^2)^2 \) also increases with the difference between cationic sizes. It must also be noted that the (Tl—Rb)NO3 and (Na—Ag)NO3 systems, the \( \Delta E \) values of which are practically linear with composition, present nearly linear equivalent conductivity isotherms.

The negative equivalent conductivity excess together with the positive activation energy excess indicate that the electrical transport is more hindered in mixtures than in the pure components. The nitrate anion is easily polarizable and when inserted between cations of different radii will experience a net, permanent, electrical field. The resulting anion polarization increases the attraction between the nitrate and the smaller cation. These conditions will result in a higher resistance for the smaller cation to move relatively to the nearest nitrate; or, in other words, the mobility of the small cation relative to the nitrate will be reduced. Internal mobility measurements in this system could be of interest just from this point of view.

We are indebted to F. Benuzzi and R. Di Cola of CETIS (Ispra) who performed the mathematical refinement of the data with the 360 IBM computer. We wish also to thank G. Bertozzi and G. Soldani, who permitted us the use of their apparatus for density measurements at high temperatures.


On the Growth of Ice in Aqueous Solutions Contained in Capillaries

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The growth rate of ice in supercooled water and in dilute aqueous solutions of various salts which dissociate in water into univalent ions was studied. The solutions contained in polyethylene tubes of small bore had concentrations between 10^{-3} and 10^{-1} moles liter^{-1} and were investigated at bath supercoolings between 1^\circ \text{C} and 15^\circ \text{C}. The growth rate of ice which in pure water was found to vary approximately with the square of the bath supercooling was affected in a systematic manner by the type and concentration of the salt in solution. At salt concentrations smaller than 5 \times 10^{-2} moles liter^{-1} most salts did not affect the growth rate. However, the fluorides were found to increase the growth rate over and above the one in pure water. At concentrations larger than 5 \times 10^{-2} moles liter^{-1} all the salts reduced the growth rate of ice below the one in pure water. By comparing solutions of salts with common cation it was found that at a particular bath supercooling and salt concentration the growth rate of ice was reduced most in lithium solutions and least in cesium and ammonium solutions. By comparing solutions of salts with common cation it was found that the growth rate of ice was reduced most in fluoride solutions and least in bromide solutions. It was concluded that in solutions with salt concentrations larger than 5 \times 10^{-2} moles liter^{-1} the rate of dissipation of latent heat which controls the growth rate of ice is affected in a systematic manner by the freezing point lowering effects which result from pure mass transfer conditions prevailing at the ice-solution interface of a stagnant system. Some features of the observed growth rates are discussed in terms of the effect of dissolved salts on the growth forms of ice in aqueous solutions.

The problem of determining the growth rates and the growth forms of ice in water and aqueous solutions has occupied the interest of many scientists since the end of the 19th century. Although the main importance of this problem lies in the realm of physical chemistry, recent studies in the...